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ERRATUM.

P. 209. To title of paper *add* "Communicated by Sir J. J. Thomson, F.R.S."

PROCEEDINGS OF
THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

On the Viscous Flow in Metals, and Allied Phenomena.

By E. N. DA C. ANDRADE, B.Sc., Physics Research Scholar, University College, London.

(Communicated by Prof. F. T. Trouton, F.R.S. Received March 9,—Read April 14, 1910.)

It has been observed* that for a lead wire, loaded well beyond the elastic limit, the extension after some time becomes proportional to the time, or the flow becomes viscous in character. The rate of this viscous flow varies with the load, and the following work was undertaken to investigate the law of this variation, and the phenomenon in general.

Methods of Experiment. The Hyperbolic Weight.

The experiments were all done on wires of the metal, and the preliminary observations were all made on lead. To suspend the wires, they were soldered into stout brass hooks. In the first rough experiments the extension registered itself on a clockwork-driven drum; these experiments showed that the rate of extension for a given load became constant for a time, but finally increased, and continued increasing. This is due to two causes: (1) As the wire stretches, the length of wire being experimented on at any moment increases. (2) As the wire stretches, the cross-section diminishes, and thus the load per unit area or stress increases. This is by far the more disturbing cause, since, as shown later, the rate increases much more rapidly with the stress than would be given by a linear law. To

* *E.g.*, Trouton and Rankine, "On the Stretching and Torsion of a Lead Wire beyond the Elastic Limit," 'Phil. Mag.' October, 1904.

obviate this difficulty an automatic method of keeping the stress constant was devised.

Constant stress was obtained by letting the weight producing the stress sink into a liquid (fig. 1) as the wire stretched, the form of the weight being so chosen that the upthrust at any moment was such that the effective load

was inversely as the length of the wire at that moment, and thus was directly as the cross-sectional area. The required shape is easily shown to be given by a hyperbola of revolution,

$$y = \sqrt{\frac{Ml_0}{\rho\pi}} \cdot \frac{1}{l_0 + x},$$

where M is the mass of the load, l_0 the initial length of the wire, and ρ the density of the liquid. As water was always used as the liquid, ρ is fixed. Having chosen a particular M and l_0 , the exact size of the weight is given. From the equation we see that a weight, once constructed, is only exactly efficient for one particular initial load, but with reasonable approximation the same weight can be used over a limited range of loads.

An additional advantage accruing from the device of the hyperbolic weight was soon discovered, viz., that stresses could be freely applied much greater than can possibly be used with constant loading. The possibility of working at much greater known stresses than is otherwise feasible opens up a new region for experiment.

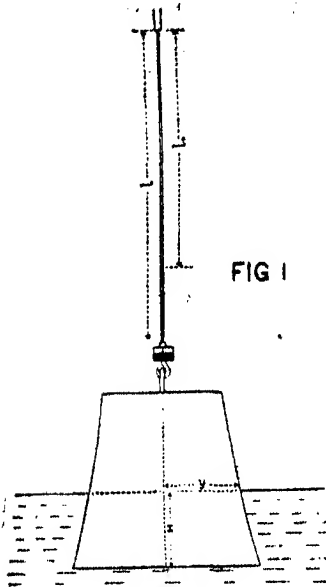
Description of Experiments.

Experiments were made on three kinds of wires:—

- (1) Approximately pure lead.
- (2) "Fuse wire." An alloy of lead and tin.
- (3) Approximately pure copper.

Fuse wire was used, because it shows the viscous flow to a remarkable extent; copper as being a metal usually supposed not to show a viscous flow.

The first experiments were made on lead. The preliminary tests were made on ordinary commercial wire; the last specimen, here called lead D,



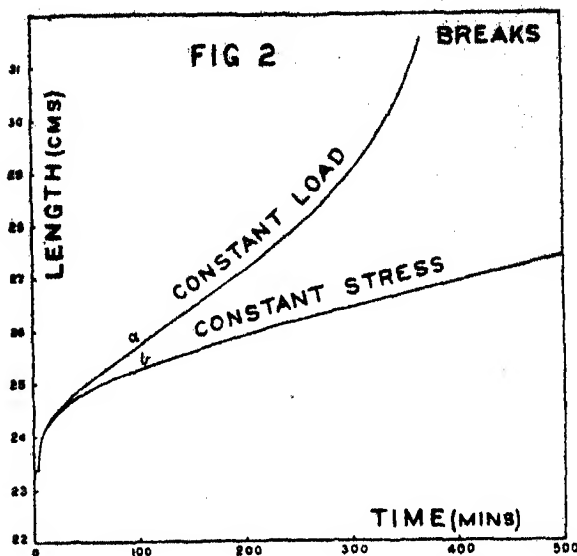
was supplied as pure lead by the London Electric Wire Company. Most of the numerical results here given were obtained from this specimen, which on analysis was found to be 99·8 per cent. pure lead. The analysis was kindly done for me by Mr. I. G. Rankin, B.Sc., who also analysed the fuse wire, and found it contained lead, 21·5 per cent.; tin, 78·5 per cent.

To observe the extension a cathetometer reading to 0·01 mm. was used. The water into which the hyperbolic weight sank was contained in a vessel of much larger diameter than the weight, filled up to the level of a hole in the side, through which the displaced water escaped, thus securing constant level. The weight was adjusted so as just to touch the surface by observation of the image in the water, the weight being previously dry; this was to avoid uncertainty caused by the surface-tension rise. Three different hyperbolic weights were used to cover the range of loads for the lead, a fourth for the fuse wire, and a fifth in the high temperature experiments, which were done with lead at 162° C.

In these experiments the temperature was maintained by an oil bath kept at constant temperature by a Riechert regulator. The wire was pulled upwards, the lower hook being hooked on to a horizontal bar running across the bottom of the bath. Short lengths of lead wire were used, about 10 cm., so that the temperature throughout might be constant, and the load was applied by a fine steel wire running over two pulleys, to which was attached a hyperbolic weight. The friction of the steel wire on the pulleys was less than 10 grammes weight.

Experimental Results.—The general nature of the stretch in a lead wire loaded beyond the elastic limit has been noted by previous workers.* An immediate extension is followed by a continuous stretch which decreases in rapidity to a final rate, constant if the extension is sufficiently small to make negligible the increase in stress due to thinning. The first result from the use of the hyperbolic weight was that even for large extensions the rate settles down to a constant value, if the stress is kept constant. In fig. 2 the extensions are shown in the two cases of constant load and constant stress for the same initial length, and the same initial load. It is to be noted that even when the stress is kept constant we should expect the rate of flow to increase again, owing to the length flowing at any moment increasing with the time; this effect, however, would not be very noticeable in the case shown, as the rate of flow at the constant stage is not very rapid. In the case of fuse wire, however, where the viscous rate is large, this effect is marked. It was found that taking the rate at different times in the viscous flow, and dividing by the mean length pertaining to each rate,

* Trouton and Rankine, *loc. cit.*



a rate per unit length was obtained, which was constant at different stages of the flow. It was thus established that *under constant stress* the rate per unit length, once the initial effect has died out, is constant right up to breaking.*

A series of results for lead under constant stress at various stresses was obtained. The experiments at high temperatures gave similar extension curves, but the initial effect was much less marked. In the extension curves for fuse wire the initial effect was smaller still; the increase in viscous rate, owing to increasing length, can be easily seen in fig. 3.

I was led to dividing the extension into three parts:—

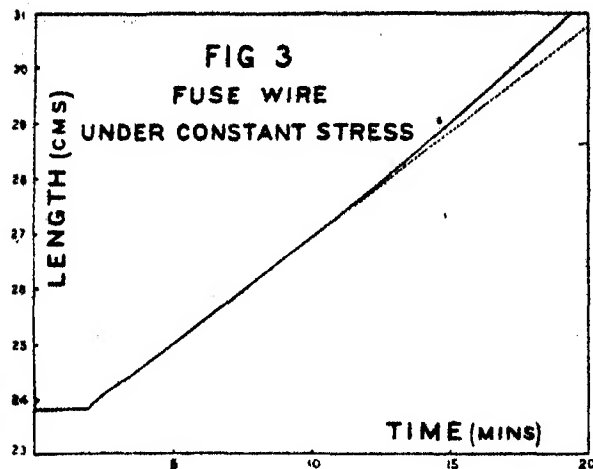
- (1) The immediate extension on loading.
- (2) An initial flow which gradually disappears.
- (3) A constant flow, taking place throughout the extension.

I shall call (2) the β -flow, as a measure of it is given by the constant β in an equation to be dealt with later. The constant flow per unit length has already been mentioned as viscous flow. A discussion of a conception of the mechanism of these flows is given in the theoretical section.

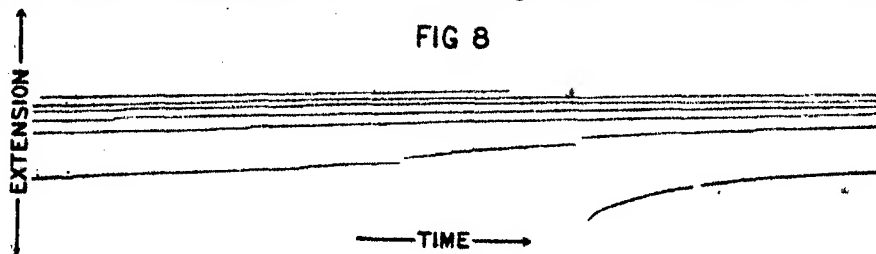
A few experiments were done on copper with the automatic recorder before mentioned. P. Phillips† states that “the copper wires made no attempt

* Breaking in such a case is merely due to a cumulative local thinning at some initial irregularity; in the case of fuse wire an extension of more than 50 per cent. of the original length was frequently obtained.

† “The Slow Stretch in Indiarubber, Glass, and Metal Wires, when subject to a Constant Pull,” P. Phillips, M.Sc., ‘Phil. Mag.’ April, 1905.



towards approximation to a linear function"; I found, however, that *when loaded near the breaking stress*, annealed copper wires gave a linear flow which was still continuing after seven days. A peculiarity of copper wire was that it showed sudden slips at irregular intervals, which, perhaps, may be called "copper quakes," as being analogous to the geological slipping supposed to result in earthquakes. These were not due to the recording apparatus. In fig. 8, which represents one of the tracings from the drum, both these



slips and the existence of a final viscous flow are evident. In copper, the viscous flow is very small, the immediate extension very large in comparison to a metal such as lead:

Before considering variations with the stress, it was thought advisable to obtain an equation to the curve of length against time at constant stress, to see how to divide up the effect into initial flow and viscous flow. For large values of the time, the length l is given by $l = Ce^{kt}$, where C is approximately constant, since, experimentally, $\frac{1}{l} \frac{dl}{dt} = \text{constant}$.

Since Phillips gives $l = a + b \log t$ for the case when there is no viscous flow, i.e. when $k = 0$, I tried

$$l = A(a + b \log t)e^{kt}.$$

This was not very successful. After various attempts, $l-l_0 = At^k$ was found to give a good representation of the initial part of the curve; the form of equation

$$l = l_0(1 + \beta t^k) e^{At}$$

was therefore attempted. This fitted our lead curves surprisingly accurately throughout the whole range. To show the closeness of the fit, the following tables for two stresses chosen at random are given, since such divergencies as there are, are too small for convenient diagrammatic representation:—

Table I.—Lead D.

Initial load, 3600 grammes. Initial length, 38·8 cm. Average temp., 14°·5 C.

Time (in minutes).	Length observed.	Length from formula $l = (39\cdot13 + 0\cdot57^{\frac{1}{2}}\sqrt{t}) e^{0\cdot0000895t}$.	Stress.
0	38·8 +	39·13	3600
1	39·73	39·70	
2	39·87	39·85	
4	40·04	40·04	
5	40·12	40·12	
15	40·56	40·57	3597
25	40·85	40·86	
35	41·07	41·00	
40	41·17	41·18	
80	41·81	41·81	
130	42·38	42·30	3597
250	43·48	43·47	
300	43·80	43·85	3601
420	44·08	44·69	
500	45·19	45·19	3602
550	45·51	45·50	

Stress given in grammes weight per area of cross-section of unstretched wire.

Table II.—Lead D.

Initial load, 1800 grammes. Initial length, 9·9 cm. Average temp., 162° C.

Time (in minutes).	Length observed.	Length from formula $l = (9\cdot94 + 0\cdot43^{\frac{1}{2}}\sqrt{t}) e^{0\cdot0109t}$.	Stress.
0	9·9 +	9·94	1800
1	10·46	10·48	
2	10·70	10·71	
3	10·90	10·90	
5	11·27	11·26	
8	11·76	11·76	1800
10	12·08	12·08	
12	12·40	12·40	
14	12·73	12·73	
15	12·90	12·90	1800

The extension curves for fuse wire, when the stress was truly constant, were equally well represented by the formula.

Since the equation $l = l_0(1 + \beta t^k)e^{kt}$ fitted my results so well, it was thought well to try the equation $l = l_0(1 + \beta t^k)$ for the case of a pure β -flow, when there is no appreciable final viscous flow. Taking a set of readings from Phillips' paper,* the equation $l = l_0(1 + \beta t^k)$ was found to fit quite as well as his logarithmic equation. To investigate this a little further, I did one experiment on β -flow in copper. The following table exhibits the result:—

Table III.— β -Flow in Copper.

Time (in minutes).	Reading.	$3 \cdot 059 - \text{reading} = l - l_0$.	$0 \cdot 131^2/\sqrt{t}$.
0	Loaded		
2	2·924	0·165	0·165
3	2·900	0·189	0·189
4	2·881	0·208	0·208
5	2·868	0·226	0·224
6	2·850	0·239	0·230
7	2·840	0·249	0·250
8	2·827	0·262	0·262
9	2·814	0·275	0·273
10	2·807	0·282	0·282
15	2·767	0·322	0·322
20	2·740	0·349	0·355

Phillips states that there were considerable deviations from the logarithmic law when the stretch had become very slow, but, unfortunately, he does not state in which direction the deviations were, so it cannot be surmised whether my formula would afford a better fit.

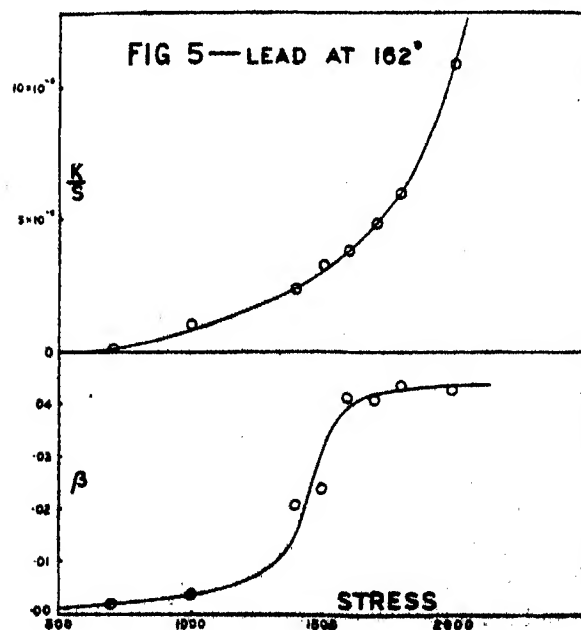
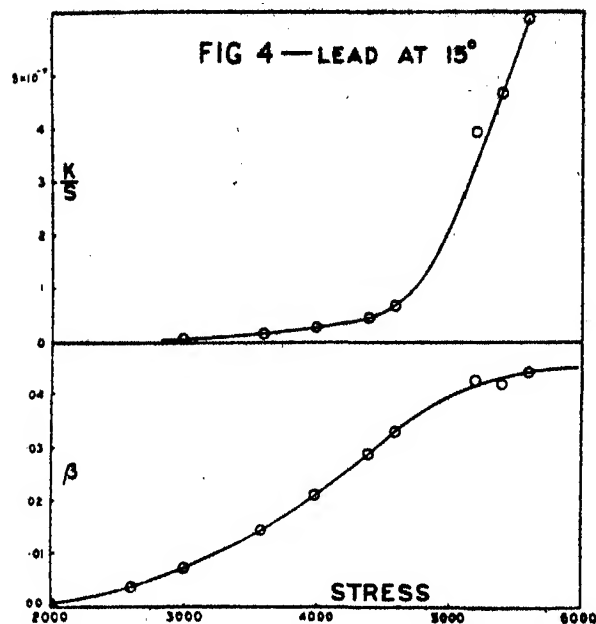
The tables given, which are representative, suffice to show, I think, that $l = l_0(1 + \beta t^k)e^{kt}$ is successful in representing the observed facts. l_0 is not the exact unstretched length, but a number slightly larger, probably the immediate length on loading, which could not be measured. β being fairly small compared to 1, $1 + \beta t^k$ becomes nearly constant for large values of t , as t^k then increases very slowly. We have for convenience called that part of the flow represented by the coefficient β the β -flow; k is a measure of the purely viscous flow.

To see how β and k varied with the stress, β and the quantity $k/(\text{stress})$, or the "fluidity," were plotted against stress. Fig. 4 shows β and $k/(\text{stress})$ for lead D at 15° , and fig. 5 the same quantities for lead D at 162° . It is to be especially noted that β tends to become constant for large values of the stress.

A form of curve similar to our β -curves was found by Phillips† for th

* *Loc. cit.*, p. 525.

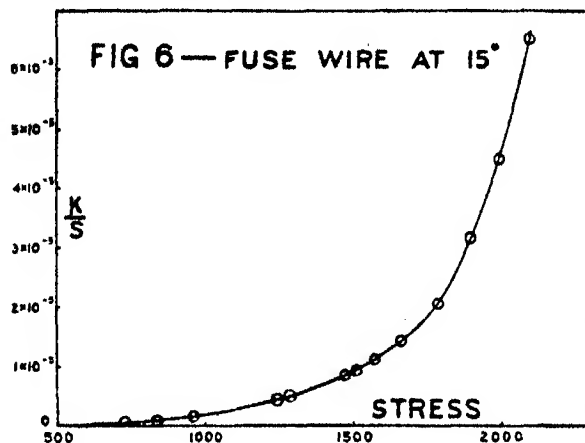
† *Loc. cit.*, p. 526. Curves III a, b, c, d.



variations of his coefficient b with the stress in his experiments on copper, where he was dealing with a case involving no sensible viscous flow. (Owing to the similarity of our equations, b and β are measures of approximately

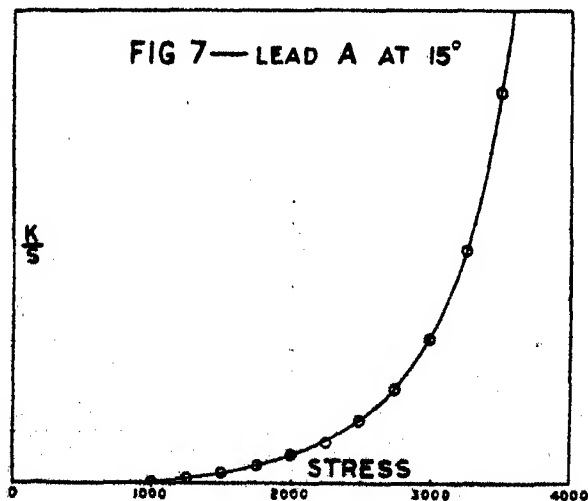
the same effect.) It is remarkable that β tends to the same limit in the experiments at 162° as in those at 15° , though the corresponding values of k are very much greater in the former case.

Fig. 6 shows the variations of k/s (where s is the stress) for fuse wire. It is of exactly the same character as in lead. β is not here shown, as it is so



small in the case of fuse wire that satisfactory determinations were not made. The curves of k/s against s can be approximately fitted by hyperbolæ having one asymptote parallel to the axis of s , and the other asymptote inclined at an acute angle to this axis.

Fig. 7 shows k/s for an early specimen of lead, A. k was computed from the later readings of the extension, it being assumed that the β -flow had died out. The values are therefore only approximate; the figure is given as a



confirmation of the character of the fluidity curve, the specimen being a softer lead than D.

Table IV.—Lead D.

Stress = s in grammes/initial area.	β .	k .	$\frac{k}{s} \times 10^6$.
Temperature, 15° C.			
2000	0·0008		
2600	0·0044		
3000	0·0077	0·000035	1·16
3600	0·0145	0·000069	1·92
4000	0·0210	0·000110	2·75
4400	0·0290	0·000202	4·60
4600	0·0334	0·000322	7·00
5200	0·0424	0·00207	40·0
5400	0·0420	0·00253	47·0
5600	0·0440	0·00345	61·6
Temperature, 162° C.			
700	0·002	0·0001	14
1010	0·0045	0·00095	94
1400	0·021	0·0032	280
1500	0·024	0·0048	320
1600	0·041	0·0060	375
1700	0·041	0·0083	488
1800	0·043	0·0106	588
2000	0·043	0·0216	1080

Approximate cross-sectional area of unstretched wire = 2·16 sq. mm.

Table V.—Fuse Wire. Temperature, 15° C.

Stress in grammes per initial area.	k .	$\frac{k}{s} \times 10^6$.
730	0·00072	1·0
840	0·00116	1·4
960	0·00197	2·05
1250	0·00590	4·7
1280	0·00628	4·9
1480	0·0132	8·9
1505	0·0146	9·7
1580	0·0174	11·0
1680	0·0241	14·3
1790	0·0369	20·6
1885	0·060	31·8
1985	0·090	45·0
2090	0·136	65·0

Approximate cross-sectional area of unstretched wire = 0·64 sq. mm.

Theoretical Considerations.

There appears to have been but little previously written on the flow in metals which will aid in formulating a theory to accord with these results. Boltzmann's well-known paper on "Elastische Nachwirkung"* offers no help. It is interesting, however, to consider the phenomena from the point of view suggested by Ewing in his Presidential Address to Section G of the British Association on the structure of metals.† In this he insists upon the crystalline nature of the structure.

We may look at the initial flow as resulting from the addition to a permanent viscous flow of a flow which dies out with the time. This latter may be taken as arising from a rearrangement or rotation of small parts of a crystalline nature in the material, much after the fashion of the rotation seen in Ewing's magnetic model illustrating hysteresis in iron; the β -curve is of the same form as the curve of magnetisation. I assume the rotation of the crystals to be opposed by some kind of elastic force proportional to the displacement, but, as in the magnetic model, a succession of equilibrium positions is passed, through which return is not spontaneously possible on the removal of the stress. The viscous flow may be regarded as taking place in a viscous matrix, in which the crystals are embedded.

If we take the formula $l = l_0(1 + \beta t^{\frac{1}{2}}) e^{kt}$, we may write

$$\frac{dl}{dt} = kl + \frac{1}{2} l_0 \beta t^{-\frac{1}{2}} + \frac{1}{2} k \int_0^t \frac{1}{2} l_0 \beta t^{-\frac{1}{2}} dt,$$

since β and kt are small within the range.‡ The first term represents a purely viscous flow, the second the flow due to rearrangement or rotations, if we assume that the number of crystals rotating per unit time diminishes as $t^{-\frac{1}{2}}$. The third term, which is small, may be regarded as a small correction to the permanent flow arising from the rotations increasing the amount of material which at any moment is in a suitable attitude for purely viscous flow: it is proportional to the number of crystals which have rotated. (The formula is not presumed to do more than represent the phenomena throughout any convenient experimental range; for very large values of t it is incorrect, as it would give the number of crystals rotating in an infinite time as being infinite. $t^{\frac{1}{2}}$ should probably be replaced by a function of t which approximates

* L. Boltzmann, 'Wiener Sitzungsberichte,' October, 1874.

† J. A. Ewing, 'Report of the British Association,' 1906, p. 657.

‡ For example, take lead for stress 4600 grammes per initial area. Here the largest value of kt was 0.079,

$$dl/dt = 0.0065 + 0.0054(1 + 0.079 + \frac{1}{2}(0.079)^2 + \dots),$$

and the omission of squares and higher powers of kt makes an error of about 0.15 per cent. in the flow.

12 *On the Viscous Flow in Metals, and Allied Phenomena.*

closely to $t^{\frac{1}{2}}$ for such values as are here considered, but which as t increases ultimately becomes constant.)

The fact that β tends to the same limit at both 162° and 15° is significant, as suggesting that the division of the flow into β -flow and viscous flow is valid physically, β -flow being dependent on a purely geometrical arrangement in the structure of the metal. Such a process as the rotations suggested would give the experimentally observed constancy of β for large stresses.

The following is a brief summary of the paper:—

(1) Establishment of the existence of a viscous flow in lead, in a lead-tin alloy, and in copper.

(2) Realisation of the necessity of working at constant stress, and the device of the "hyperbolic weight" for this purpose.

(3) Demonstration that at constant stress the flow is purely viscous right up to breaking for the metals used.

(4) The empirical formula $l = l_0(1 + \beta t^{\frac{1}{2}})e^{kt}$ is shown to fit very closely all the extension-curves. The flow can be divided into β -flow and viscous flow.

(5) The β -flow is experimentally shown to tend to a limit for large stresses.

(6) The β -flow is shown to tend to the same limit at 162° as at 15° C.

(7) The curve of fluidity against stress is shown to be roughly a hyperbola, with one asymptote parallel to, and the other steeply inclined to, the stress axis.

It is a great pleasure to me to offer my thanks to Prof. Trouton, to whose unremitting kindness and encouragement whatever merit there may be in this work is largely due. I also owe my thanks to Assistant-Professor A. W. Porter for many suggestions, and for reading through the paper.

*The Refraction and Dispersion of Argon, and Redeterminations
of the Dispersion of Helium, Neon, Krypton, and Xenon.*

By CLIVE CUTHBERTSON, Fellow of University College, London, and
MAUDE CUTHBERTSON.

(Communicated by Prof. F. T. Trouton, F.R.S. Received March 16,—Read
April 14, 1910.)

So far as we are aware only four determinations of the refractivity of argon
have been published. These are as follows:—

Observer.	Wave-length.	$(\mu-1)10^7$.	Remarks.
Rayleigh*	White	2808	} Assuming the value 2022 for air ($\lambda = 5894$). The results for these and four other lines are expressed by $\mu-1 =$ $0.0002792 + \frac{1.6 \times 10^{-14}}{\lambda^2}$.
Ramsay and Travers†	"	2828	
Burton‡	6563	2829	
	5896	2837	
Ahrberg§	6439	2796	
	5790-70	2803	
	5461	2816	
	4359	2851	

* 'Roy. Soc. Proc.,' vol. 59, p. 203.

† 'Roy. Soc. Proc.,' vol. 64, p. 190, and vol. 67, p. 331.

‡ 'Roy. Soc. Proc.,' A, vol. 80, p. 390.

§ Ahrberg, 'Inaug. Diss. Halle,' 1909.

The first two determinations only deal with the refraction of white light, while the value of Ahrberg's results is limited by the fact that he was only able to count 12 bands in the red and 50 bands at the other points selected; so that his whole dispersion effect must have been about one band in the violet, a number which is insufficient to ensure great accuracy. Another determination may not, therefore, be considered superfluous.

The specimen of argon used by us was kindly lent by Sir William Ramsay, by whom it was purified. The spectrum showed a trace of hydrogen, but none of other gases. The mean of seven experiments gave a refractive index of 1.00028230 for the wave-length 5461. These determinations varied between 1.00028258 and 1.00028183. The dispersion was measured for the seven wave-lengths 6438.5 (Cd), 5790.5 (Hg), 5769.5 (Hg), 5460.7 (Hg), 5209.1 (Ag), 5085.8 (Cd), 4799.9 (Cd).

The first two columns of the following table show the results. The refractivity is here doubled in order to facilitate comparison with the diatomic gases:—

Table I.—Dispersion of Argon.

$\lambda \times 10^8$.	Observed $(\mu-1) 10^2$.	Calculated.	Difference.
6438.5	56173	56174	+1
5790.5	56346	56346	0
5769.5	56345	56353	+8
5460.7	56480	56459	-1
5209.1	56559	56560	+1
5085.8	56612	56615	+3
4799.9	56764	56760	-4

For the reasons given in a previous paper* the dispersion formula $\mu-1 = C/(n_0^2-n^2)$ was adopted; and the values of the constants were calculated, by the method of least squares, from all the determinations except that for λ 5769.5, which was evidently affected by error (a cause for which could be assigned). The value of C was found to be 9.43264×10^{27} and of n_0^2 to be 17008.9×10^{27} . The numbers calculated from this formula are given in Column 3 and the differences between the calculated and observed results are shown in Column 4. It will be seen that the *relative* refractivities for different wave-lengths can generally be trusted to one or two points in the fifth significant figure. In these experiments the number of bands read (λ 5461) varied between 300 and 400, and the discrepancy between observation and experiment corresponds to an error of less than one-fiftieth of an interference band, a degree of accuracy greater than there was reason to expect.

Our values of the constants compare as follows with the results of Burton and Ahrberg when their figures are expressed in the formula used by us:—

Observer.	$C \times 10^{-27}$.	$n_0^2 \times 10^{-27}$.
Burton	9.124	16335
Ahrberg	7.437	13516
C. and M. Cuthbertson	9.43264	17008.9

Although we had recently published determinations of the refractive indices of the other inert gases, we were tempted by the improvement† in the source of light and in the disposition of our apparatus to repeat observations on them in order to bring them all up to the same level of accuracy.

Table II shows the experimental results (doubled as in the case of argon).

* 'Roy. Soc. Proc.' vol. 83, p. 152.

† We used Dr. T. M. Lowry's arc with poles of cadmium and silver alloy. By substituting for one electrode an alloy of silver and lithium, kindly made for us by Messrs. Johnson and Matthey (about 98 per cent. Ag, 2 per cent. Li), we were able to use the lithium line λ 6707.85 in the later experiments.

The figures given in the columns "calculated" were derived from the constants of the equation

$$\mu - 1 = C/(n_0^2 - n^2)$$

shown in Table III, which were calculated from the observations by the method of least squares. It will be found that the discrepancies between the observed and calculated results are of the same order as in the case of argon. The maximum number of bands read in the case of each element is given in the same table. The figures given in large type are the absolute values of the refractivities for λ 5461 which were assumed for the calculation of the dispersion. They were not redetermined, but taken from our previous measurements.

Table II.—Redeterminations of the Dispersion of Helium, Neon, Krypton, and Xenon. $(\mu - 1) \times 10^8$.

$\lambda \times 10^3$	Helium.		Neon.		Krypton.		Xenon.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
6707·85	—	—	—	—	85066	85055	13946	13946
6488·5	6972·6	6972·8	13403	13402	85160	85168	13974	13973
5790·6	6983·4	6983·1	13421	13420	85522	85518	14055	14056
5769·5	6963·8	6983·5	13421	13421	85529	85531	14058	14059
5460·7	6990·0	6989·8	13432	13431	85748	85747	14109·8	14110
5209·1	6996·2	6995·9	13442	13442	85955	85953	14158	14159
5085·8	6998·4	6999·1	13446	13448	86068	86066	14185	14185
4799·9	7008·0	7007·8	13462	13462	86361	86363	14257	14256

Table III.—Refractivities of the Inert Gases.
Values of Constants in the Equation $\mu - 1 = C/(n_0^2 - n^2)$.

Element.	$C \times 10^{-27}$.	$n_0^2 \times 10^{-27}$.	Maximum number of bands read.
Helium	2·42476	84991·7	349
Neon	5·18652	38916·2	440
Argon	9·43264	17008·9	400
Krypton	10·6893	12767·9	430
Xenon	12·2418	8977·87	550

It is satisfactory to find that the values of n_0^2 now obtained by these more accurate measurements do not differ in any case by more than 2 per cent. from the values published by us in September last.*

For the loan of all these gases we have to thank Sir William Ramsay, and we have also pleasure in recording our obligations to Prof. Trouton, and to the Royal Society for a grant.

* 'Roy. Soc. Proc.,' A, vol. 83, p. 149, 1909.

The Total Ionisation produced in Different Gases by the Cathode Rays ejected by X-Rays.

By R. D. KLEEMAN, D.Sc., B.A., McKinnon Student of the Royal Society, Emmanuel College, Cambridge.

(Communicated by Prof. W. H. Bragg, F.R.S. Received March 25,—Read June 2, 1910.)

It is probable that the energy necessary to make an ion from any given atom does not depend much on the nature of the ionising agent or on its penetrating power. But no direct experiments have yet been made to test this point, except those described in this paper. The quantity usually measured is the ionisation produced in different gases by an ionising agent when it is completely absorbed. The total ionisation may then be expressed as the product of two factors: (i) the average ionisation per unit length of path of the rays, and (ii) the total distance traversed; or, the total ionisation produced when the energy of the ionisation falls from E_1 to E_2 , where $(E_1 - E_2)$ is small, is equal to the product of the ionisation per unit length by the distance traversed.

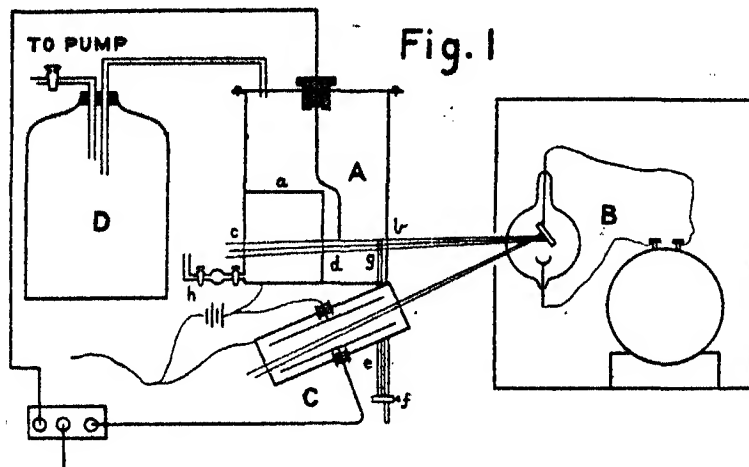
The writer has carried out some experiments on the ionisation produced per centimetre in various gases by the β -rays of uranium and actinium.* The velocity of the β -rays of actinium is less than that of the β -rays of uranium, for the penetrating power of the latter, as measured by their absorption in aluminium, is about double that of the former. But it was found that the relative ionisations in different gases per centimetre of path are practically the same. In other words, the ratio of the ionisation per centimetre in any given gas to that in air is the same for both sets of β -rays. It seems probable, therefore, that this quantity does not depend very much on the penetrating power of the rays.

Prof. Bragg then suggested that further light might be thrown on the connection between ionisation and absorption by measurements of the total ionisation produced by cathode rays. A set of measurements was accordingly undertaken.

A diagram of the apparatus used is shown in fig. 1. A is a cylindrical ionisation chamber partitioned into two by the lead wall a . The chamber was originally not designed for this experiment, but adapted to it by dividing it into two compartments. Three windows b, d, c in the same straight line enabled a beam of X-rays from the bulb B to be shot right through the

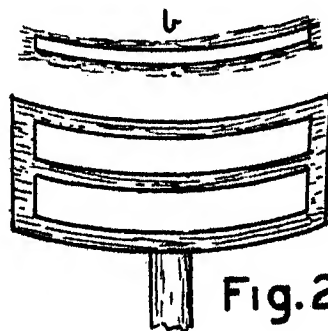
* 'Roy. Soc. Proc.,' A, vol. 83, p. 530, 1910.

chamber. The two outer windows *b* and *c* are of aluminium, and the intermediate one *d* is of tissue paper. Their dimensions are: *b*, 5 cm. by 2 mm.; *d*, 5 cm. by 2 cm.; and *c*, 6 cm. by 1 cm. A plate of brass *g*, which makes a



close sliding contact with the chamber wall, has two windows cut in it, either of which can be moved in front of the window *b*. A different view of the plate *g* and the slit *b* is shown in fig. 2. The plate is supported by the rod *e*, which can be clamped in any desired position to a fixed rod by the clamp *f*. The two windows in the brass plate were covered with a piece of cardboard about 1 mm. thick. The surface of the cardboard opposite the windows was covered with four layers of gold leaf. But in one of the windows this leaf was placed on the side of the cardboard facing the interior of the chamber, and in the other it was placed on the side nearest the wall of the chamber.

The leak in the chamber is a measure of the ionisation between d and g . It is due to the ions made in the gas by the direct action of the X-rays, and to those made by the cathode rays from whichever window of the plate g is in the path of the X-rays. When the window with the gold leaf facing the interior of the chamber is placed in the path of the X-rays, a larger amount of cathode radiation is obtained than when the other window is so placed. This is due to the fact that the absorption of X-rays by the gold is much greater than that by an equal mass of cardboard, and there is a consequent larger production of cathode rays. Moreover, the chance of a cathode ray



getting out of the material is the same in the two cases, for the scattering of the cathode rays is the same for equal masses. If, therefore, a leak is taken with the gold covered window in the path of the X-rays, and then a leak with the cardboard window only, we can, by subtracting the second from the first, obtain a leak due to the cathode radiations from the gold only, the leak due to the direct action of the X-rays on the gas disappearing in the subtraction.

In order to be independent of the variations in the intensity of the X-rays a standard chamber C was used. The leak in the chamber A when the X-ray bulb was working was measured directly by an electrometer while the leak in the chamber C was stored up. The electrometer was then discharged and connected with the chamber C, and its charge measured. The ratio of the two deflections is independent of the intensity of the X-rays and of the time of leak.

The cathode rays ejected by X-rays are absorbed by a few millimetres of air at atmospheric pressure. Now the distance across the chamber from *g* to *d* is 4 cm. Therefore, unless the pressure is very low, the cathode rays are entirely absorbed by the gas. Thus the above measurements give the total ionisation produced by the cathode rays.

The method of filling the chamber with the gas under examination is described in detail in the author's paper quoted above. In brief, the chambers A and B were exhausted down to a few millimetres pressure by means of a Fleuss pump, and the liquid was allowed to evaporate into the apparatus by the arrangement shown at *h*. The remnant of air in the chamber is swept by the vapour into the chamber D.

Experimental Results.

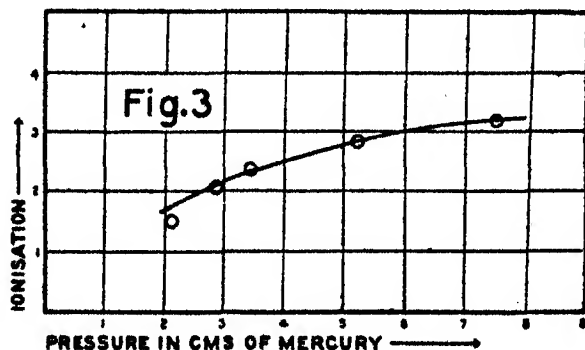
Measurements carried out in the manner described show that if we confine ourselves to gases whose molecules contain no atoms heavier than oxygen, the total ionisation is practically independent of the pressure. There was just a slight increase as the pressure was increased, but not sufficiently large or definite to be taken account of. But with gases containing atoms heavier than oxygen the total ionisation increased with pressure. Such an effect would be obtained if the gold radiates soft X-rays in addition to the cathode rays. This would have the effect of superposing on the constant ionisation due to the cathode rays an extra amount of ionisation proportional to the pressure. The curve connecting ionisation and pressure would, therefore, slope up as the pressure is increased.

It is evident that the slope of the curve is dependent on the rate of absorption of the X-rays in the gas.

In light gases the absorption is very small, and hence this upward slope

is also very small. But in heavy gases the absorption is very much greater. Thus, according to Crowther, the ionisations in $\text{C}_2\text{H}_5\text{Br}$ and CH_3I are 72 and 145 times as great as the ionisation in air. This upward tendency is therefore very much greater in such gases, and its effect was well marked. It was found that in gases containing chlorine atoms the increase of ionisation with pressure is practically linear. The total ionisation caused by the cathode rays, since they are in each case totally absorbed, is given by the intercept of this line on the ionisation axis. The total ionisation in gases containing chlorine was determined in this way. The correction thus introduced amounted to about 20 or 30 per cent.

But with gases containing bromine and iodine the increase of ionisation with pressure was much larger and was not linear. It was, therefore, impossible to obtain a value for the total ionisation of the cathode rays in these gases. Moreover, the experiments were rendered difficult from the fact that the ionisation produced by the direct action of the primary X-rays on the gas was greater than that produced by the cathode radiations from the gold. In the case of the light gases the opposite was the case. The apparent total ionisation of CH_3I in terms of that in air is plotted in fig. 3. The intercept on the ionisation axis is the total ionisation due to the cathode rays. This could, however, not be determined from the curve.



The curve resembles a saturation curve; the maximum ionisation ordinate would give the sum of the total ionisations produced by the cathode rays and by the secondary X-rays. The shape of the curve must depend to a certain extent on the cathode radiation of high velocity ejected from the gas. But we see that the maximum ordinate would be about twice the intercept on the axis. This means that the energy liberated in the form of soft X-rays is of about the same order as that liberated in the form of cathode rays. When a light gas, such as air, is used the effect due to the soft X-rays is less than one-hundredth of that due to the cathode rays.

i.e., in a chamber of the dimensions of that used in these experiments. A similar curve was obtained with ethyl bromide, but it did not rise so rapidly with the pressure. Both the methyl iodide and the ethyl bromide curves indicate that the relative total ionisation for the cathode rays probably lies between 1 and 2.

The experimental results are now given in Table I. The total ionisations obtained by Prof. Bragg* with the α -particle are also placed in the table for comparison. It will be seen that they are almost exactly the same as obtained by the writer with the cathode rays.

Now, the total ionisation is equal to the product of the length of path traversed by the ionising agent when its energy falls from E_1 to E_2 , into the ionisation per unit length of path. The relative ionisation per unit length does not seem to depend on the velocity of the β -rays according to the experiments by the writer on the ionisation by the β -rays of actinium and uranium (*loc. cit.*), and this probably holds therefore down to cathode rays. This is shown by Table II, which also contains the ionisations per unit length of path obtained by Prof. Bragg for the α -particle. It appears from this table, then, that the ionisations for the α -particle are approximately the same as for the β -rays of actinium or uranium for gases which contain no atoms heavier than chlorine. Therefore, since total ionisation = ionisation per centimetre \times length of path, the relative distances traversed in different gases when the energy falls from E_1 to E_2 are probably the same for the α -particle and for cathode rays. Now, the distance traversed by the α -particle is inversely as the sum of the square roots of the atomic weights of the constituent atoms of the molecule, and this law therefore probably holds also for cathode rays in gases which contain no heavier atoms than chlorine. The path of the cathode ray, will, however, not be a straight line.

Apart from any relations between the length of path traversed by the α -particle and by the cathode ray for a given decrease of energy, the equality between the numbers representing the total ionisations indicates that the energy necessary to ionise an atom is the same for the α -particle as for the cathode ray. The writer has shown† that the electron ejected by an α -particle has a component of motion in the direction of motion of the α -particle, and that therefore part, at least, of the energy of ionisation is derived from the kinetic energy of the α -particle. It follows, therefore, that probably the same amount of energy of ionisation is derived from the ionising cathode ray.

* 'Trans. Roy. Soc. of South Australia,' October, 1906.

† 'Roy. Soc. Proc., A, vol. 83, p. 195, 1909.

Table I.

Name of gas.	Total ionisation by cathode rays.	Total ionisation by the α -particle.
Air.....	1.00	1.00
Carbon dioxide, CO_2	1.08	1.08
Ethyl oxide, $\text{C}_2\text{H}_5\text{O}$	1.23	1.32
Pentane, C_5H_{12}	1.31	1.35
Benzene, C_6H_6	1.20	1.29
Ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$	1.33	1.32
Chloroform, CHCl_3	1.34	1.29
Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$	Probably lying between 1 and 2	
Methyl iodide, CH_3I		

Table II.

Gas.	Ionisation by the α -particles of radium.	Ionisation by the β -rays of uranium.	Ionisation by the β -rays of actinium.
Air	1.00	1.00	1.00
O_2	1.15	1.17	
CO_2	1.59	1.60	
$\text{C}_2\text{H}_5\text{O}$	2.14	2.12	
C_5H_{12}	4.85	4.55	
CH_3O	1.74	1.69	
$\text{C}_2\text{H}_5\text{O}$	4.40	4.39	4.28
C_5H_8	4.30	3.95	
$\text{C}_2\text{H}_5\text{Cl}$	3.12	3.24	3.24
CHCl_3	4.08	4.94	
CCl_4	5.28	6.28	
CS_2	2.99	3.62	
CH_3I	3.43	5.90	5.11

Table III.

Atoms.	Atomic ionisation.	Atomic stopping power.	Relative energy spent per ion.
H	0.175	0.132	0.754
C	0.51	0.436	0.894
N	0.47	0.493	1.05
O	0.55	0.530	0.962
S	1.24	0.745	0.803
Cl	1.16	0.785	0.876
Br	1.72	1.18	0.885
I	2.26	1.43	0.638
H^+	0.116	0.182	1.14

Other Work on the Subject.

It will be of interest to give here a short summary of and discussion upon the work that has been done on total ionisation, and the energy necessary to make an ion.

The energy necessary to make an ion relative to that required to make an ion in air is not always independent of the nature of the parent atom nor of chemical combination. If S denotes the stopping of a gas for an α -particle, then the range of the particle is $1/S$. The total ionisation caused by the particle is then given by $T = I/S$, where I is the ionisation per centimetre of path. Further, the energy necessary to make a single ion E is inversely proportional to the total number of ions made. Therefore we get $E = S/I$.

Now, the stopping power as regards α -rays is additive in all gases, being, in fact, proportional to the sum of the square roots of the masses of the atoms.* The ionisation per centimetre is also approximately additive in all gases tried except hydrogen.† We may therefore assume that the atoms involved would have the same stopping power and atomic ionisation in the free state as they have when combined, and that these quantities are additive. The values of E may therefore be calculated for these atoms, using the values of S and I determined from compounds obeying the additive law. This equation has in this way been applied by the writer (*loc. cit.*) to α -particle ionisation data given by*Prof. Bragg.‡ The results are given in Table III. It will be seen that the relative energy necessary to make an ion is not independent of the nature of the parent atom. The differences are much greater than could possibly be accounted for by experimental error. Since the total ionisation obtained with the cathode rays is the same as with the α -particle, these values also apply when the ion is made by a cathode ray.

The stopping power of the hydrogen atom is normal, that is, the same amount of energy is expended upon an atom of pure hydrogen as when the hydrogen is combined in a compound. But the ionisation per centimetre in hydrogen is less than that deduced from the additive law. The energy spent in making an ion in pure hydrogen will be given as before by dividing the stopping power of the atom by the ionisation per atom deduced from measurements in hydrogen itself. The energy deduced in this way is placed under H^* in the table. It will be seen that it is much greater than the

* Bragg and Kleeman, 'Phil. Mag.,' September, 1905.

† Kleeman, 'Roy. Soc. Proc.,' A, vol. 79, 1907.

‡ 'Trans. Roy. Soc. of South Australia,' October, 1906.

other value obtained when the hydrogen atom occurs in a compound containing other atoms besides hydrogen atoms.

The absolute amount of energy necessary to make an ion cannot be less than a certain value, viz., the work done in separating two electrical charges from a distance apart equal to the radius of the molecule to an infinite distance. This work is e^2/r , which becomes 1.16×10^{-11} erg if we put $e = 3.4 \times 10^{-10}$ and $r = 10^{-8}$ cm. All the best determinations of the energy necessary to make an ion give a value of this order.

When an atom is ionised the electron must possess an amount of kinetic energy equal to the above to enable it to get away from the positive atom. But besides this it probably has an additional quantity of energy sufficient to make its temperature equal to that of the parent atom. The mass of an electron given by the equation $e/m = 1.84 \times 10^7$ is 6.1×10^{-28} gramme. If the mass of a hydrogen molecule is taken as 14.2×10^{-26} gramme, and its velocity of translation at 0° C. as 185,900 cm. per second, then we have $v^2 \times 6.1 \times 10^{-28} = 14.2 \times 10^{-26} \times (185,900^2)$, where v is the additional velocity of the electron. This equation gives $v = 9 \times 10^6$ cm. per second. The energy corresponding to this velocity is 2.47×10^{-14} erg, which is small in comparison with the energy expended in separating the electron from its parent atom.

It is of interest to note that the slow cathode particles set free by the α -particle and by cathode rays have a velocity of 3.4×10^6 cm. per second, and this velocity is independent of the nature of the metal which emits them.* The kinetic energy corresponding to this velocity is 3.5×10^{-12} erg, which is of the same order of magnitude as the energy necessary to make an ion.

Rutherford and McClung† have determined the energy necessary to make an ion by X-rays on the assumption that all the energy absorbed is expended in ionisation. The energy of the rays was measured by their heating effect. They obtained for the energy necessary to make an ion the value 19.6×10^{-11} erg. This value is probably too high, for according to Barkla a large amount of energy is dissipated in the form of scattered radiation.

A gas at a high temperature undergoes considerable ionisation. Equilibrium is reached when the number of ions formed is equal to the number lost by recombination. The thermodynamics of such a process, which has been worked out by Gibbs and others, gives an equation connecting the work of dissociation or ionisation with other known quantities. This relation has been used by H. A. Wilson‡ to determine the energy of ionisation from

* Füchtbauer, 'Ann. d. Phys.,' p. 301, June, 1907.

† 'Phil. Trans.,' A, vol. 196, p. 25, 1902.

‡ 'Phil. Trans.,' A, vol. 197, p. 415, 1901.

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measurements of the conductivity of a gas. He obtained the value 2.8×10^{-12} erg in this way.

Townsend,* in his experiments on ionisation by collision, was able to determine from the electric field applied the velocity of the electron when it produced an ion by collision. This velocity he found to be 2.7×10^8 cm. per sec. He thus obtained the value 2.3×10^{-11} erg as the energy necessary to produce an ion. This velocity is of the same order as the thermal velocity of agitation of an electron at a temperature of the order of 1000° C. Possibly at high temperatures the free ions in matter might produce fresh ions merely by their velocity of agitation.

Stark found from other data the value 5.1×10^{-11} erg, while Langevin gives the value 10.1×10^{-11} erg.

Rutherford† has determined the energy necessary to make an ion by the α -particle. Knowing the heating effect of a gramme of radium and the number of α -particles ejected, the kinetic energy of an α -particle was calculated to be 4.7×10^{-6} erg. Now 48 per cent. of the kinetic energy is spent on ionisation, and since an α -particle produces about 86,000 ions, the energy necessary to make an ion becomes 2.7×10^{-11} erg.

I wish to thank Prof. Bragg for his kind and inspiring interest in these experiments.

* 'Phil. Mag.,' vol. 6, 1, p. 198, 1901.

† 'Radio-activity,' second edition.

*The Incidence of Light upon a Transparent Sphere of Dimensions
Comparable with the Wave-Length.*

By LORD RAYLEIGH, O.M., F.R.S.

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In a paper, now nearly thirty years old,* I applied Maxwell's equations of the electro-magnetic field to investigate the disturbance produced by an obstacle upon plane waves of light which travel through a medium otherwise uniform, giving particular attention to the case where the properties of the obstacle differ but little from those of its surroundings. The difference may consist in a variation of K — the specific inductive capacity, or of μ — the magnetic capacity, or of both; but it was shown that the last supposition leads to results inconsistent with observation, and that the evidence favours the view that μ is to be treated as invariable. Denoting electric displacements by f, g, h , the primary wave was taken to be

$$h_0 = e^{int} e^{ikx}, \quad (23)$$

so that the direction of propagation is along x (negatively), and that of vibration parallel to, z . $\Delta\mu$ being omitted, the electric displacements (f_1, g_1, h_1) in the scattered wave, so far as they depend upon the *first power* of ΔK , have at a great distance the values

$$f_1, g_1, h_1 = \frac{k^2 KP}{4\pi r} \left(\frac{\alpha\gamma}{r^2}, \frac{\beta\gamma}{r^2}, -\frac{\alpha^2 + \beta^2}{r^2} \right), \quad (35, 37, 38)$$

in which $P = \iiint h_0 \Delta K^{-1} e^{-ikr} dx dy dz. \quad (36)$

In these equations r denotes the distance between the point (α, β, γ) , where the disturbance is required to be estimated, and the element of volume of the obstacle $dx dy dz$.

It is evidently implied that in a direction $(\alpha = 0, \beta = 0)$ parallel to that of primary vibration, the scattered vibration vanishes, whatever may be the size and shape of the obstacle, so that any light which may appear in this direction must depend upon powers of ΔK higher than the first.

If ΔK be uniform throughout the obstacle, it may be removed from under the integral sign in (36), and if the value of K for the external medium be taken as unity, we may write

$$K\Delta K^{-1} = -(K-1).$$

* 'Phil. Mag.,' vol. 12, p. 81, 1881; 'Scientific Papers,' vol. 1, p. 518. In the second term of Equation (32) and following, ΔK^{-1} should read $\Delta\mu^{-1}$.

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If the obstacle is very small, h_0 and r may be treated as constants in the integration, and

$$P = -(K-1) h_0 e^{-ihr} \cdot T, \quad (40)$$

if T be the whole volume of the small obstacle. Using this in (35), etc., we get

$$f_1, g_1, h_1 = \frac{\pi T (K-1)}{\lambda^2 r} e^{i(nt-kr)} \left[-\frac{\alpha\gamma}{r^2}, -\frac{\beta\gamma}{r^2}, \frac{\alpha^2 + \beta^2}{r^2} \right], \quad (41, 42, 43)$$

λ being the wave-length ($2\pi/k$). These equations apply, whatever may be the shape of the small obstacle; and, of course, they undergo no change if the shape be spherical. In that case it was shown that the restriction upon the value of $K-1$ may be removed, provided we replace $K-1$ by $3(K-1)/(K+2)$.

We have seen that the scattered light vanishes to a first approximation in $(K-1)$ for the direction parallel to z . In the case of the sphere it was shown that for this direction we have to a second approximation for a small obstacle

$$f_2 = \frac{\pi T (K-1)^2}{\lambda^2 r} e^{i(nt-kr)} \cdot \frac{k^2 R^2}{25}, \quad (60)$$

with $g_2 = 0, h_2 = 0$. In (60) R denotes the radius of the sphere, and r is measured from the centre. "Comparing (60) and (41) we see that the amplitude of the light scattered along z is not only of higher order in ΔK , but is also of the order $k^2 R^2$ in comparison with that scattered in other directions. The incident light being white, the intensity of the component colours scattered along z varies as the inverse eighth power of the wave-length, so that the resultant light is a rich blue." It is obvious from (41) that in general the intensity of the scattered light varies as λ^{-4} .

"There is another point of importance to be noticed. Although when the terms of the second order are included, the scattered light does not vanish along the axis of z , the peculiarity is not lost but merely transferred to another direction. Putting together the terms of the first and second orders we see that the scattered light will vanish in a direction in the plane of xz , inclined to z (towards $+x$) at a small angle θ , such that

$$\theta = \frac{\Delta K}{K} \frac{k^2 R^2}{25} = (K-1) \frac{k^2 R^2}{25}." \quad (61)$$

Some experiments in illustration were then described.

Returning to the case where $(K-1)^2$ is neglected, we consider a spherical obstacle of any radius R , whose centre is at the origin of co-ordinates. From (23), (36)

$$P = -(K-1) e^{int} \iiint e^{ik(x-r)} dx dy dz,$$

r being the distance between $dx dy dz$, and the (distant) point at which f_1, g_1, h_1 are to be estimated. It is evident that, so far as the secondary ray is concerned, P depends only upon the angle (χ) which this ray makes with the primary ray. We will suppose that $\chi = 0$ in the direction backwards along the primary ray, and that $\chi = \pi$ along the primary ray continued. The integral may then be found in the form

$$\frac{2\pi R^2 e^{-ikr_0}}{k \cos \frac{1}{2}\chi} \int_0^{\frac{1}{2}\pi} J_1(2kR \cos \frac{1}{2}\chi \cos \phi) \cos^2 \phi d\phi; \quad (48)$$

r_0 being the distance of the point of observation from the centre of the sphere. If we expand the Bessel's function and drop the suffix in r_0 as no longer required, we get

$$P = -\frac{4\pi R^3 (K-1) e^{i(nt-kr)}}{3} \left\{ 1 - \frac{m^2}{2.5} + \frac{m^4}{2.4.5.7} - \frac{m^6}{2.4.6.5.7.9} + \frac{m^8}{2.4.6.8.5.7.9.11} - \dots \right\}, \quad (49)$$

in which m is written for $2kR \cos \frac{1}{2}\chi$. From this f_1, g_1, h_1 follow at once by (35), etc. Along the continuation of the primary ray $\cos \frac{1}{2}\chi = 0$, and P reduces to

$$-\frac{4\pi}{3} R^3 (K-1) e^{i(nt-kr)},$$

as was to be expected. It is to be observed that in this solution there is no limitation upon the value of R if $(K-1)^2$ is neglected absolutely.

Prof. Love, in a valuable paper on the "Scattering of Electric Waves by a Dielectric Sphere,"* has treated this problem by a different method, limited on the one hand to the sphere, but on the other applicable whatever may be the value of $(K-1)$, and (so far as the general analytical expressions are concerned) whatever may be the size of the sphere. In the 1881 paper I had treated in this way the problem of a dielectric *cylinder*. From these expressions Love deduces first and second approximations applicable when the radius of the sphere may be treated as small in comparison with the wave-length. It will be of interest to compare these approximations with those already referred to.

In Prof. Love's notation the electric forces are represented by X, Y, Z ; and, so far as relates to the medium outside the sphere, they may be identified with f, g, h used above. The co-ordinates of the point of observation are denoted by x, y, z instead of by α, β, γ . Again, Love supposes the direction of propagation to be along $-z$ (instead of $-x$), and the direction of

* 'Lond. Math. Soc. Proc.,' vol. 30, p. 308, 1899.

vibration to be parallel to y (instead of z), changes represented by taking one step backwards in the cycle x, y, z, x . Thus (with omission of a constant multiplier which runs through) the primary wave is represented by

$$Y = e^{ik(ct+x)}. \quad (X)$$

Corresponding to this, the complete expressions, so far as terms of order $k^4 R^5$, for the forces in the scattered wave at a great distance are found to be

$$\begin{aligned} (X, Y, Z) = & \frac{K-1}{K+2} \frac{k^2 R^3 e^{ik(ct-r+R)}}{r} \left(-\frac{xy}{r^2}, \frac{x^2+z^2}{r^2}, -\frac{yz}{r^2} \right) \\ & \times \left\{ 1 - ikR - k^2 R^2 \left(\frac{19}{18} - \frac{6}{5} \frac{K}{K+2} \right) \right\} \\ & + (K-1) \frac{k^4 R^5 e^{ik(ct-r+R)}}{30 r} \left(0, -\frac{z}{r}, \frac{y}{r} \right) \\ & + \frac{K-1}{2K+3} \frac{k^4 R^5 e^{ik(ct-r+R)}}{6 r} \left(0, -\frac{z}{r}, \frac{y}{r} \right) \\ & + \frac{K-1}{2K+3} \frac{k^4 R^5 e^{ik(ct-r+R)}}{3 r} \frac{yz}{r^2} \left(\frac{x}{r}, \frac{y}{r}, \frac{z}{r} \right). \quad (XLII) \end{aligned}$$

So far as the first approximation involving $k^2 R^3$, this agrees *mutatis mutandis* with (41, 42, 43), since $T = \frac{4}{3}\pi R^3$ and $k = 2\pi/\lambda$.

We may next consider the application of (XLII) to the secondary ray in the direction of primary vibration ($x = 0, z = 0, y = r$), for which the first approximation vanishes. We have

$$\begin{aligned} (X, Y, Z) = & \frac{(K-1) k^4 R^5 e^{ik(ct-r)}}{30 r} \left[(0, 0, 1) + \frac{5}{2K+3} (0, 0, -1) \right] \\ = & \frac{(K-1)^2 k^4 R^5 e^{ik(ct-r)}}{15 (2K+3) r} (0, 0, 1); \end{aligned}$$

and this agrees with (60) when we introduce the supposition that $(K-1)$ is small, so that $2K+3$ in the denomination may be identified with 5.

I have already commented upon this agreement;* but recently in pursuing the comparison I came upon a discrepancy. It is evident from the theory already given that a great general simplification should attend the supposition that $(K-1)$ is very small. Introducing this into (XLII) and omitting for the moment the factor

$$(K-1) k^2 R^3 \frac{e^{ik(ct-r+R)}}{r},$$

we find for the three last sets of terms

$$-\frac{k^2 R^2}{15} \frac{z}{r} \left(-\frac{xy}{r^2}, \frac{x^2+z^2}{r^2}, -\frac{yz}{r^2} \right),$$

* 'Scientific Papers,' vol. 1, p. 536, 1899.

showing within the bracket the same dependence on x, y, z as does the first set. Hence altogether, expanding the exponential e^{ikR} , we may write in this case

$$(X, Y, Z) = \frac{(K-1)k^2R^2e^{ik(ct-r)}}{3r} \left(-\frac{xy}{r^2}, \frac{x^2+z^2}{r^2}, -\frac{yz}{r^2} \right) \\ \times \left\{ 1 + k^2R^2 \left(\frac{1}{2} - \frac{1}{3} + \frac{2}{3} \right) - \frac{k^2R^2}{5} \frac{z}{r} \right\}.$$

This should correspond with (35), (49) of the former investigation if in the latter we stop at the term in m^2 where

$$m^2 = 4k^2R^2 \cos^2 \frac{1}{2} \chi = 2k^2R^2 \left(1 + \frac{z}{r} \right),$$

so that
$$P = -\frac{4\pi R^3(K-1)e^{i(n\tau - kr)}}{3} \left\{ 1 - \frac{k^2R^2}{5} \left(1 + \frac{z}{r} \right) \right\}.$$

It will be seen that in all respects except one the agreement is complete. For example, i has disappeared otherwise than as contained in $e^{ik(ct-r)}$. But there remains a numerical discrepancy, since $(\frac{1}{2} - \frac{1}{3} + \frac{2}{3})$ is not equal to $-\frac{1}{5}$.

For some time I was at a loss to account for this discrepancy, until I noticed that the omission of a term $\frac{2}{15}k^2R^2$ in Love's equation (XXXIV) would produce harmony, and this led me to scrutinise equation (XVIII), where (I believe) the error lies. It appears to me that these equations should be

$$\left. \begin{aligned} \phi_n &= \frac{ik e^{ikct}}{n(n+1)\psi_n(kR)} \left[\frac{R^2}{2n+3} \psi_{n+1}(kR) \frac{dV_{n+1}}{dx} \right. \\ &\quad \left. - \frac{r^{2n+1}}{2n-1} \psi_{n-1}(kR) \frac{d}{dx} \left(\frac{V_{n-1}}{r^{2n-1}} \right) \right], \\ \chi_n &= -\frac{ik e^{ikct}}{n(n+1)\psi_n(kR)} \left[\frac{R^2}{2n+3} \psi_{n+1}(kR) \frac{dV_{n+1}}{dy} \right. \\ &\quad \left. - \frac{r^{2n+1}}{2n-1} \psi_{n-1}(kR) \frac{d}{dy} \left(\frac{V_{n-1}}{r^{2n-1}} \right) \right], \end{aligned} \right\} \text{(XVIII*)}$$

the change consisting in the substitution of $(2n+3)$ for $(2n+1)$ in the denominators of the first terms of ϕ_n, χ_n . We should then obtain

$$\chi_1 = -\frac{1}{2} ik e^{ikct} y \text{ simply,}$$

instead of (XXXIV), which involves also the factor $(1 + \frac{2}{15}k^2R^2)$. This is a matter to which I shall presently return.

In view of numerical calculations, it may be well to complete the statement of Prof. Love's results, and to show that, especially when corrected as above, they admit of considerable simplification.

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For the functions which occur in (XVIII) we have $V_0 = 1$, and for n greater than unity

$$V_n = \frac{(ikr)^n}{1.3.5 \dots (2n-1)} P_n\left(\frac{z}{r}\right), \quad (\text{XIV})$$

P_n denoting as usual Legendre's function, so that V_n is a solid harmonic of degree n . For ψ_n we have

$$\begin{aligned} \psi_n(\eta) &= (-)^n 1.3.5 \dots (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta}\right)^n \frac{\sin \eta}{\eta} \\ &= 1 - \frac{\eta^2}{2.2n+3} + \frac{\eta^4}{2.4.2n+3.2n+5} - \frac{\eta^6}{2.4.6(2n+3)(2n+5)(2n+7)} \\ &\quad + \dots, \quad (\text{IV})^* \end{aligned}$$

and the functions $\psi_n(\eta)$ satisfy certain sequence equations which may be written

$$\frac{1}{\eta} \frac{d}{d\eta} \psi_n(\eta) = -\frac{\eta^2}{2n+3} \psi_{n+1}(\eta) = (2n+1) \{\psi_{n-1}(\eta) - \psi_n(\eta)\}. \quad (\text{VI})$$

We have also to deal with another function, $E_n(\eta)$, such that

$$E_n(\eta) = (-)^n 1.3.5 \dots (2n+1) \left(\frac{1}{\eta} \frac{d}{d\eta}\right)^n \frac{e^{-i\eta}}{\eta}, \quad (\text{VII})$$

and the functions $E_n(\eta)$ satisfy the same sequence equations as the functions $\psi_n(\eta)$. It will be seen that $-i\psi_n(\eta)$ is the imaginary part of $E_n(\eta)$. As included in (VII),

$$E_0(\eta) = \frac{e^{-i\eta}}{\eta}, \quad E_1(\eta) = 3 \frac{1+i\eta}{\eta^3} e^{-i\eta}. \quad (\text{XXXVI})$$

This being understood, the disturbance in the secondary wave, so far as it depends upon ϕ_n, χ_n , may be written

$$\begin{aligned} X_n &= M_n E_n(kr) \left(y \frac{d\phi_n}{dz} - z \frac{d\phi_n}{dy} \right) \\ &+ \frac{N_n}{ik} \left[-(n+1) E_{n-1}(kr) \frac{d\chi_n}{dx} + \frac{nk^2 r^{2n+3}}{(2n+1)(2n+3)} E_{n+1}(kr) \frac{d}{dx} \frac{\chi_n}{r^{2n+1}} \right], \quad (\text{XV}) \end{aligned}$$

with two similar equations for Y_n, Z_n . The complete expressions for X, Y, Z involve a summation with respect to n which takes the values 1, 2, 3, etc.

All is now defined except the constants M_n, N_n , which depend upon the boundary conditions to be satisfied at the surface of the sphere. For the present case of a dielectric sphere of refractive index \sqrt{K} , or k/k , Prof. Love finds the equivalent of

$$\begin{aligned} M_n &= \frac{\psi_{n-1}(kR) - \frac{\psi_{n-1}(k'R)}{\psi_n(k'R)} \psi_n(kR)}{-E_{n-1}(kR) + \frac{\psi_{n-1}(k'R)}{\psi_n(k'R)} E_n(kR)}, \quad (\text{XXIII}) \end{aligned}$$

* This series is the same as that which occurs in the expression for $J_{n+\frac{1}{2}}(\eta)$.

$$N_n = \frac{K\psi_{n-1}(kR) - \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(k'R)}{\psi_n(k'R)} \right\} \psi_n(kR)}{-KE_{n-1}(kR) + \left\{ (K-1) \frac{n}{2n+1} + \frac{\psi_{n-1}(k'R)}{\psi_n(k'R)} \right\} E_n(kR)}, \quad (\text{XXIII bis})$$

which completes the analytical solution.

Returning now to (XVIII*) we see that the first terms dV_{n+1}/dx , dV_{n+1}/dy are solid harmonics of degree n . Also V_{n-1}/r^{2n-1} is a solid harmonic of degree $-n$. When differentiated with respect to x or y , it becomes a solid harmonic of degree $-n-1$, and when further multiplied by r^{2n+1} , a solid harmonic of degree n . Hence both terms in (XVIII*) are solid harmonics of degree n , and it will appear (as might, indeed, be anticipated) that they are of the same form. Writing μ for z/r , we have from (XIV)

$$\frac{dV_{n+1}}{dx} = \frac{(ik)^{n+1} r^{n-1} x}{1.3.5 \dots (2n+1)} \left\{ (n+1) P_{n+1}(\mu) - \mu \frac{dP_{n+1}}{d\mu} \right\}. \quad (a)$$

Again

$$r^{2n+1} \frac{d}{dx} \frac{V_{n-1}}{r^{2n-1}} = \frac{(ik)^{n-1} r^{n-1} x}{1.3.5 \dots (2n-3)} \left\{ -nP_{n-1}(\mu) - \mu \frac{dP_{n-1}}{d\mu} \right\}. \quad (b)$$

Now (Todhunter's 'Laplace's Functions,' pp. 43, 46) the quantities within { } in (a) and (b) are equal to one another and to $-dP_n/d\mu$, so that

$$r^{2n+1} \frac{d}{dx} \frac{V_{n-1}}{r^{2n-1}} = -\frac{(2n-1)(2n+1)}{k^2} \frac{dV_{n+1}}{dx}, \quad (c)$$

and

$$\begin{aligned} \frac{R^2}{2n+3} \psi_{n+1}(kR) \frac{dV_{n+1}}{dx} - \frac{r^{2n+1}}{2n-1} \psi_{n-1}(kR) \frac{d}{dx} \frac{V_{n-1}}{r^{2n-1}} \\ = \frac{dV_{n+1}}{dx} \frac{2n+1}{k^2} \left\{ \frac{k^2 R^2}{2n+1.2n+3} \psi_{n+1}(kR) + \psi_{n-1}(kR) \right\} \\ = \frac{dV_{n+1}}{dx} \frac{2n+1}{k^2} \psi_n(kR), \end{aligned}$$

by (VI). We thus obtain the greatly simplified forms

$$\phi_n, \chi_n = \frac{(2n+1) ik^{-1} e^{ikt}}{n.n+1} \left\{ \frac{dV_{n+1}}{dx}, -\frac{dV_{n+1}}{dy} \right\}, \quad (d)$$

in which R does not appear at all.

Referring to (XIV) and introducing the value of $P_n(z/r)$, we find

$$\left. \begin{aligned} V_0 &= 1, & V_2 &= -\frac{1}{6} k^2 (2z^2 - x^2 - y^2), \\ V_1 &= ikz, & V_3 &= -\frac{ik^3}{30} \{2z^3 - 3z(x^2 + y^2)\}. \end{aligned} \right\} \quad (\text{XXVI})$$

Thus in the case of $n = 1$ we have

$$\chi_1 = -\frac{1}{2} iky e^{ikt},$$

without any approximation depending on the smallness of R .

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For further reductions it will be convenient to introduce a modified form of V_n , viz. U_n , defined by

$$V_n = \frac{(ik)^n U_n}{1.3.5 \dots (2n-1)} = \frac{(ikr)^n}{1.3.5 \dots (2n-1)} P_n\left(\frac{z}{r}\right). \quad (\text{XIV}^*)$$

We have now to consider the solution expressed in (XV), and we may at once introduce the simplifying condition that r is very great. In this case from (VII)

$$E_n(kr) = i^n . 1.3.5 \dots (2n+1) \frac{e^{-ikr}}{(kr)^{n+1}}; \quad (\text{XXVIII})$$

and we find from (XV), (d)

$$X_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n.n+1.kr^{n+1}} \left[M_n \left(y \frac{d}{dz} - 2 \frac{d}{dy} \right) \frac{dU_{n+1}}{dx} - N_n \left(r \frac{d}{dx} - \frac{nx}{r} \right) \frac{dU_{n+1}}{dy} \right]; \quad (e)$$

and in the cyclical changes by which Y and Z are deduced from X , dU_{n+1}/dx , dU_{n+1}/dy are to stand unaltered.

For systematic calculation it is best to express U_{n+1} in terms of P . As in (a)

$$\frac{dU_{n+1}}{dx} = x r^{n-1} \{ (n+1) P_{n+1} - \mu P'_{n+1} \} = -x r^{n-1} P'_n; \quad (f)$$

so that we may write

$$\frac{dU_{n+1}}{dx}, \frac{dU_{n+1}}{dy} = -(x, y) r^{n-1} P'_n. \quad (g)$$

The differential coefficients which appear in (e) are now readily formed. We find

$$X_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n.n+1.kr} \frac{xy}{r^2} [-M_n P''_n - N_n (P'_n + \mu P''_n)], \quad (h)$$

$$Y_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n.n+1.kr} \left[M_n \left(-\mu P'_n + \frac{x^2}{r^2} P''_n \right) + N_n \left\{ \left(1 - \frac{y^2}{r^2} \right) P'_n - \frac{y^2}{r^2} \mu P''_n \right\} \right] \quad (i)$$

$$Z_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n.n+1.kr} \frac{y}{r} [M_n P'_n + N_n \{ -\mu P'_n + (1 - \mu^2) P''_n \}]. \quad (j)$$

The $\{ \}$ in (j) may alternatively be written $\mu P'_n - n(n+1) P_n$, in virtue of the differential equation satisfied by P_n .

It should be observed that the above values satisfy $xX_n + yY_n + zZ_n = 0$, as of course they ought to do.

At this stage it may be convenient to write down the values of P'_n for the earlier values of n .

	P'_n
$n = 1$	1
$n = 2$	3μ
$n = 3$	$-\frac{3}{2} + \frac{8.5}{2}\mu^2$
$n = 4$	$-\frac{8.5}{2}\mu + \frac{5.7}{2}\mu^3$

Thus from (h), (i), (j),

$$X_1, Y_1, Z_1 = \frac{3 e^{ik(ct-r)}}{2 \cdot kr} \left[-\frac{xy}{r^2} N_1, -\mu M_1 + N_1 \left(1 - \frac{y^2}{r^2} \right), \frac{y}{r} (M_1 - \mu N_1) \right];$$

$$X_2, Y_2, Z_2 = -\frac{5 e^{ik(ct-r)}}{2 \cdot kr} \left[-\frac{xy}{r^2} (M_2 + 2\mu N_2), M_2 \left(1 - 2\mu^2 - \frac{y^2}{r^2} \right) + \mu N_2 \left(1 - \frac{2y^2}{r^2} \right), \right. \\ \left. \frac{y}{r} \{ \mu M_2 + N_2 (1 - 2\mu^2) \} \right];$$

$$X_3 = \frac{7 e^{ik(ct-r)}}{4 \cdot kr} \frac{xy}{r^2} \left\{ -5 \mu M_3 + N_3 \left(\frac{1}{2} - \frac{3.5}{2} \mu^2 \right) \right\},$$

$$Y_3 = \frac{7 e^{ik(ct-r)}}{4 \cdot kr} \left[\mu M_3 \left\{ \frac{1}{2} - \frac{3.5}{2} \mu^2 + 5 \left(1 - \frac{y^2}{r^2} \right) \right\} \right. \\ \left. + N_3 \left\{ \left(1 - \frac{y^2}{r^2} \right) \left(\frac{3.5}{2} \mu^2 - \frac{1}{2} \right) - 5 \mu^2 \right\} \right]$$

$$Z_3 = \frac{7 e^{ik(ct-r)}}{4 \cdot kr} \cdot \frac{y}{r} \left[M_3 \left(\frac{5}{2} \mu^2 - \frac{1}{2} \right) + \mu N_3 \left(\frac{11}{2} - \frac{15}{2} \mu^2 \right) \right];$$

$$X_4 = -\frac{9 e^{ik(ct-r)}}{4 \cdot kr} \frac{xy}{r^2} \left[M_4 \left(\frac{3}{2} - \frac{3.7}{2} \mu^2 \right) + N_4 (3\mu - 14\mu^3) \right],$$

$$Y_4 = -\frac{9 e^{ik(ct-r)}}{4 \cdot kr} \left[M_4 \left\{ -\frac{7}{2} \mu^4 + \frac{3}{2} \mu^2 - \frac{y^2}{r^2} \left(\frac{3}{2} - \frac{3.7}{2} \mu^2 \right) \right\} \right. \\ \left. + N_4 \left\{ \frac{7}{2} \mu^3 - \frac{3}{2} \mu + \frac{y^2}{r^2} (3\mu - 14\mu^3) \right\} \right],$$

$$Z_4 = -\frac{9 e^{ik(ct-r)}}{4 \cdot kr} \frac{y}{r} \left[M_4 \left(\frac{7}{2} \mu^3 - \frac{3}{2} \mu \right) + N_4 \left(-14\mu^4 + \frac{3.9}{2} \mu^2 - \frac{3}{2} \right) \right].$$

Our expressions naturally simplify when we limit ourselves to secondary rays which lie in the principal planes. No real loss of generality is thereby incurred, since whatever may be the direction of primary vibration, that vibration may be resolved into two, respectively in and perpendicular to the plane which contains the primary and secondary rays. Thus, if $y = 0$, that

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is for secondary rays whose direction is perpendicular to that of primary vibration, we have generally $X_n = 0$, $Z_n = 0$, and

$$Y_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n \cdot n+1 \cdot kr} [M_n \{\mu P'_n - n(n+1)P_n\} + N_n P'_n]. \quad (k)$$

Again, if $x = 0$, that is for secondary rays lying in the plane which contains the directions of primary vibration and propagation, $X_n = 0$, and

$$Y_n = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n \cdot n+1 \cdot kr} [-M_n \mu P'_n - N_n \mu \{\mu P'_n - n(n+1)P_n\}],$$

while Z_n retains the form (j). The direction of vibration is in the plane $x = 0$, and is, of course, perpendicular to the secondary ray. Its magnitude is given by

$$\frac{yZ_n - zY_n}{r} = \frac{(-)^{n+1}(2n+1)e^{ik(ct-r)}}{n \cdot n+1 \cdot kr} [M_n P'_n + N_n \{\mu P'_n - n(n+1)P_n\}]. \quad (l)$$

It will be seen that (k) and (l) differ only by an interchange of M_n , N_n .

It may be remarked that when $\mu = \pm 1$, (k) and (l) should become identical, except as to sign. If $\mu = -1$, the signs are the same; if $\mu = +1$, they are opposite. Thus when $\mu = \pm 1$, the [] in (l) becomes $P'_n (M_n \mp N_n)$ simply. And in this case by the differential equation,

$$\mu P'_n = \frac{1}{2} n(n+1) P_n.$$

When n is even, $P_n = 1$, and then $P'_n = \pm \frac{1}{2} n(n+1)$; when n is odd, $P_n = \pm 1$, and then $P'_n = \frac{1}{2} n(n+1)$.

Accordingly, (l) gives in the case of $\mu = \pm 1$,

$$\frac{yZ - zY}{r} = \frac{e^{ik(ct-r)}}{kr} \left[\frac{3}{2} M_1 + \frac{5}{2} N_2 + \frac{7}{2} M_3 + \frac{9}{2} N_4 + \dots \right. \\ \left. \mp \left(\frac{3}{2} N_1 + \frac{5}{2} M_2 + \frac{7}{2} N_3 + \frac{9}{2} M_4 + \dots \right) \right], \quad (m),$$

the upper sign in the anbiguities relating to $\mu = +1$.

Arranged in powers of μ the general expression from (l) as far as M_5 , N_5 inclusive is

$$\frac{yZ - zY}{r} = \frac{e^{ik(ct-r)}}{kr} \left[\frac{3}{2} M_1 - \frac{5}{2} N_2 - \frac{7}{8} M_3 + \frac{27}{8} N_4 + \frac{11}{16} M_5 \right. \\ + \mu \left\{ -\frac{3}{2} N_1 - \frac{5}{2} M_2 + \frac{77}{8} N_3 + \frac{27}{8} M_4 - \frac{11 \cdot 29}{16} N_5 \right\} \\ + \mu^2 \left\{ 5 N_2 + \frac{35}{8} M_3 - \frac{9 \cdot 27}{8} N_4 - \frac{77}{8} M_5 \right\} \\ + \mu^3 \left\{ -\frac{7 \cdot 15}{8} N_3 - \frac{9 \cdot 7}{8} M_4 + \frac{33 \cdot 21}{8} N_5 \right\} \\ + \mu^4 \left\{ \frac{9 \cdot 7}{2} N_4 + \frac{11 \cdot 21}{16} M_5 \right\} - \mu^5 \frac{11 \cdot 105}{16} N_5 \left. \right]. \quad (n),$$

The corresponding expression for Y from (k) is derivable by interchange of M and N .

When $\mu = 0$, we have in (l) to consider

$$M_n P'_n - n(n+1) N_n P_n.$$

In this when n is odd, $P_n(0) = 0$ and $P'_n(0)$ takes in succession the values

$$1, -\frac{3}{2}, \frac{3 \cdot 5}{2 \cdot 4}, -\frac{3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6}, \frac{3 \cdot 5 \cdot 7 \cdot 9}{2 \cdot 4 \cdot 6 \cdot 8}, \text{ etc.},$$

while when n is even, $P'_n(0) = 0$, and $P_n(0)$ takes the values

$$[1], -\frac{1}{2}, \frac{1 \cdot 3}{2 \cdot 4}, -\frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6}, \frac{1 \cdot 3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6 \cdot 8}, \text{ etc.}$$

Using these in (l), we find for $\mu = 0$

$$\frac{yZ - zY}{r} = \frac{e^{ik(ct-r)}}{kr} \left[\frac{3}{2} M_1 - \frac{5}{2} N_2 - \frac{7}{2 \cdot 4} M_3 + \frac{9 \cdot 3}{2 \cdot 4} N_4 + \frac{11 \cdot 3}{2 \cdot 4 \cdot 6} M_5 \right. \\ \left. - \frac{13 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6} N_6 - \frac{15 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6 \cdot 8} M_7 + \frac{17 \cdot 3 \cdot 5 \cdot 7}{2 \cdot 4 \cdot 6 \cdot 8} N_8 + \dots \right], \quad (o)$$

and the corresponding value of Y in (k) is obtained by interchange of M and N .

We now pass on to consider the values of M_n, N_n as given in (XXIII). By (VII), when η is small, $E_n(\eta)$ is of the order $\eta^{-(2n+1)}$, so that N_n is of the order η^{2n+1} . M_n is two orders higher, viz., η^{2n+3} , since the numerator is itself a small quantity of the order η^2 . When η is small, the most important terms in X, Y, Z depend upon N_1 and are of order η^3 or R^3 . If we are satisfied with an approximation as far as R^5 inclusive, we have only to consider N_1, M_1 , and N_2 . For R^7 we need N_1, M_1, N_2, M_2, N_3 , and so on.

Let us begin by supposing that $(K-1)$ is small, and retain only the first power of this quantity. For example, in $\psi_n(k'R)$, we may write

$$\psi_n(k'R) = \psi_n(kR) + \psi'_n(kR) \cdot (k' - k) R.$$

We find, omitting for brevity the argument in $\psi_n(kR)$, etc.,

$$M_n = \frac{(K-1)kR}{2} \frac{\psi_{n-1}\psi'_n - \psi_n\psi'_{n-1}}{\psi_{n-1}E_n - \psi_nE_{n-1}}, \quad (p)$$

$$N_n = (K-1) \frac{\left(\psi_{n-1} - \frac{n}{2n+1} \psi_n \right) \psi_n + \frac{1}{2} kR (\psi_{n-1}\psi'_n - \psi_n\psi'_{n-1})}{\psi_{n-1}E_n - \psi_nE_{n-1}}, \quad (q)$$

The denominator in (p), (q) appears at first sight complex, since E is so

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If, however, we separate real and imaginary parts, writing in accordance with the definitions (IV), (VII)

$$E_n(\eta) = \Psi_n(\eta) - i\psi_n(\eta), \quad (r)$$

we see that

$$\psi_{n-1}E_n - \psi_nE_{n-1} = \psi_{n-1}\Psi_n - \psi_n\Psi_{n-1}, \quad (s)$$

from which the imaginary part has disappeared. In this case accordingly M_n, N_n are wholly real.

The denominator (s) admits of simple evaluation. By (VI)

$$\psi_{n-1}E_n - \psi_nE_{n-1} = \frac{\eta}{2n+1}(\psi'_nE_n - \psi_nE'_n).$$

Now, if V_n be a solid harmonic, the same in both cases, $V_n\psi_n$ and V_nE_n both satisfy the equation $(\nabla^2 + k^2) = 0$, and hence by Green's theorem ('Theory of Sound,' vol. 2, p. 252) as applied to the space included between two concentric spheres, we find that,

$$\psi'_nE_n - \psi_nE'_n = C_n\eta^{-2n-2},$$

where C_n is independent of η . To determine C_n we may suppose η very small, when

$$\psi_n = 1, \psi'_n = -\frac{\eta}{2n+3}, E_n = (2n+1) \frac{1^2 \cdot 3^2 \dots (2n-1)^2}{\eta^{2n+1}}.$$

Thus

$$C_n = 1^2 \cdot 3^2 \cdot 5^2 \dots (2n+1)^2,$$

$$\text{and} \quad \psi_{n-1}E_n - \psi_nE_{n-1} = 1^2 \cdot 3^2 \cdot 5^2 \dots (2n-1)^2 \times (2n+1) \eta^{-2n-1}. \quad (t)$$

It will be understood that (t) is true without approximation as regards η , if $(K-1)^2$ is neglected.

It is now a simple matter to calculate M_n, N_n to a moderately high power of η . So far as η^7 inclusive, we have

$$N_1 = \frac{2(K-1)\eta^3}{9} \left(1 - \frac{\eta^2}{5} + \frac{7\eta^4}{10 \cdot 5 \cdot 7} \right), \quad M_1 = \frac{(K-1)\eta^5}{45} \left(1 - \frac{\eta^2}{7} \right),$$

$$N_2 = \frac{(K-1)\eta^5}{5 \cdot 15} \left(1 - \frac{\eta^2}{7} \right), \quad M_2 = \frac{(K-1)\eta^7}{35 \cdot 45},$$

$$N_3 = \frac{4(K-1)\eta^7}{7 \cdot 35 \cdot 45}.$$

Thus

$$Z = Z_1 + Z_2 + Z_3 = \frac{e^{ik(ct-r)}}{kr} \cdot \frac{y}{r} \left[\frac{3}{2}M_1 - \frac{5}{2}N_2 \right. \\ \left. + \mu \left\{ -\frac{3}{2}N_1 - \frac{5}{2}M_2 + \frac{77}{8}N_3 \right\} + 5\mu^2N_2 - \frac{7 \cdot 15}{8}\mu^3N_3 \right],$$

in which $\frac{1}{2} M_1 - \frac{1}{2} N_2 = 0$, so that μ becomes a factor of the whole expression as we know it ought to do. Also

$$X = \frac{e^{ik(ct-r)}}{kr} \frac{xy}{r} \left[-\frac{3}{2} N_1 + \frac{5}{2} M_2 + \frac{7}{8} N_3 + \mu \left(5 N_2 - \frac{7 \cdot 5}{4} M_3 \right) - \frac{7 \cdot 3 \cdot 5}{2 \cdot 4} N_3 \mu^2 \right].$$

In X the multiplier of xy should be the same as the multiplier of yz in Z . In order that this may be so, we must have $M_2 = \frac{7}{4} N_3$, a relation satisfied by the tabular values. In the expression for Y , the part which does not contain the factor $1 - y^2/r^2$, or $(x^2 + z^2)/r^2$, vanishes in virtue of the relations already mentioned. Finally, arranged in powers of η , or kR ,

$$X, Y, Z = \frac{e^{ik(ct-r)} k^2 R^3 (K-1)}{3r} \left(-\frac{xy}{r^2}, \frac{x^2+z^2}{r^2}, -\frac{yz}{r^2} \right) \\ \times \left\{ 1 - \frac{1}{3} k^2 R^2 (1+\mu) + \frac{k^4 R^4}{2 \cdot 5 \cdot 7} (1+\mu)^2 \right\},$$

in agreement with (35), (49) so far as the present solution extends. The former method is incomparably the more appropriate in this particular case, giving the result for the sphere to any degree of approximation in kR , as well as admitting of application to obstacles of other forms. The general conclusion that (o) vanishes, when $(K-1)^2$ is neglected would probably be difficult to establish by the present method.

Abandoning the restriction as to the smallness of $(K-1)$, we find from (XXIII) as far as R^5 inclusive

$$N_1 = \frac{2(K-1)k^3 R^3}{3(K+2)} \left\{ 1 - \frac{3}{8} k^2 R^2 + \frac{6Kk^2 R^2}{5(K+2)} \right\}, \\ M_1 = \frac{(K-1)k^5 R^5}{45}, \quad N_2 = \frac{(K-1)k^5 R^5}{15(2K+3)}; \quad (u)$$

where it will be seen that to this order M, N are still real. The corresponding values of X, Y, Z are given by

$$X, Y, Z = \frac{3e^{ik(ct-r)}}{2 \cdot kr} N_1 \left(-\frac{xy}{r^2}, \frac{x^2+z^2}{r^2}, -\frac{yz}{r^2} \right) + \frac{3e^{ik(ct-r)}}{2 \cdot kr} M_1 \left(0, -\frac{z}{r}, \frac{y}{r} \right) \\ - \frac{5e^{ik(ct-r)}}{2 \cdot kr} N_2 \left\{ -\frac{2xyz}{r^3}, \frac{z}{r} \left(1 - \frac{2y^2}{r^2} \right), \frac{y}{r} \left(1 - \frac{2z^2}{r^2} \right) \right\}. \quad (v)$$

This agrees with Prof. Love's solution, except in the first set of terms, as already mentioned.

The special case where the secondary ray lies in one or other principal plane is given by (u) and its derivative, when the approximate values of M, N are introduced.

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When kR , or η , can no longer be treated as small, we must calculate M and N from the general formulæ (XXIII) and (XXIII bis). Separating E into its real and imaginary parts, we see that the denominator of M_n is equal to

$$-\Psi_{n-1}(\eta) + \frac{\Psi_{n-1}(\eta')}{\Psi_n(\eta')} \Psi_n(\eta) + i \times \text{numerator}.$$

Also that the numerator for N_n exceeds the numerator for M_n by

$$(K-1) \Psi_{n-1}(\eta) - (K-1) \frac{n}{2n+1} \Psi_n(\eta);$$

and that the real part of the denominator of N_n exceeds the real part of the denominator of M_n by

$$(K-1) \frac{n}{2n+1} \Psi_n(\eta) - (K-1) \Psi_{n-1}(\eta),$$

while the imaginary part of the denominator of N_n is $i \times$ the numerator of N_n . When the numerators and denominators have been computed, the values of M_n , N_n must be reduced to the standard complex form.

In selecting special cases for calculation we notice that η and η' (kR and $k'R$) are both arbitrary. With the view of reaching something distinctive, it seemed desirable to choose a refractive index (k'/k) not too small. For this purpose $k'/k = 1.5$ seemed suitable, as large enough, and yet not outside the experimental range. This corresponds to $K = 2.25$. By further choosing $\eta = 1$, $\eta = 3/2$, $\eta = 9/4$ we make the tabulation of ψ serve a double purpose.

The most obvious procedure for calculating $E_n(\eta)$, equivalent to $\Psi_n(\eta) - i \Psi_n(\eta)$, is to use the sequence formula (VI),

$$E_{n+1} = \frac{2n+1 \cdot 2n+3}{\eta^2} \{E_n - E_{n-1}\}, \quad (\text{VI})$$

starting from E_0 and E , as given by (XXXVI). So far as regards the real part, represented by Ψ , this course is satisfactory; but the same cannot be said of the application to ψ . As n increases, the successive ψ 's tend to equality, and any errors are multiplied at the next step by the large factor $(2n+1)(2n+3)$. So much is this the case that although we use seven-figure logarithms throughout, even the first figure in ψ_6 or ψ_7 becomes doubtful.

It is true that these higher orders in ψ do not need to be known very accurately, for they contribute but little to the final result; nevertheless, an improvement in the calculation is called for.

An easy escape from the difficulty is provided by the series for ψ_n given in (IV). When η is moderate, as here, and n somewhat large, the convergence is good, and we may calculate ψ_6 and ψ_6 by a perfectly straight-

forward process to a high degree of accuracy. Having obtained ψ_6 and Ψ_6 , we may then use the sequence formula (VI) in the reverse direction to deduce in turn ψ_4 , ψ_3 , etc., without loss of accuracy. The values of Ψ_n and ψ_n , calculated for the various cases, are here tabulated. It is possible that they may prove useful in kindred enquiries. From them are deduced the complex values of M and N as already explained. In this case the tables give the *logarithms* of the real and imaginary parts.

Tables of Ψ and ψ .

n.	Ψ .	ψ .	Ψ .	ψ .
	$\eta = 1.$		$\eta = 1.5.$	
0	0.54080	0.84147	0.04716	0.66499
1	4.1453	0.90351	1.3929	0.79235
2	54.075	0.98053	8.9713	0.84900
3	1747.5	0.94569	117.89	0.88121
4	—	0.95541	3049.8	0.90204
5	—	—	—	0.91664
6	—	—	—	0.92743
$\eta = 2.25.$			$\eta = 27/8.$	
0	-0.279188	0.345811	-0.288262	-0.068531
1	+0.295636	0.577175	-0.136838	+0.238183
2	+1.70318	0.685527	+0.190406	+0.403904
3	+9.73119	0.749095	+1.03318	+0.509211
4	+99.3041	0.791075	+4.61147	+0.582438
5	+1933.51	0.820928	+31.1003	+0.686441
6	+51793.7	0.843272	+332.545	+0.677969
$\eta = 2.$			$\eta = 3.$	
0	-0.208073	0.454640	-0.329997	0.047040
1	+0.525919	0.653096	-0.062959	0.345677
2	+2.75247	0.744180	+0.445063	0.407729
3	+19.4823	0.796977	+1.97564	0.591812
4	+263.495	0.831564	+10.7141	0.655080
5	+8039.32	0.856018	+96.1227	0.701448
6	+206485	0.874244	+1357.05	0.736738
$\eta = 7/4.$			$\eta = 21/8.$	
0	-0.101855	0.562278	-0.331241	0.188160
1	+0.864129	0.725411	+0.070827	0.460481
2	+4.73185	0.799021	+0.875249	0.592807
3	+44.1968	0.841250	+4.08595	0.672133
4	+811.861	0.868721	+29.3550	0.725271
5	+24315.9	0.888047	+363.049	0.763446
6	—	0.902893	—	0.792237

Tables of M and N.

n .	M_n .	N_n .
$\eta = 1.$		
1	$[2.4483] - i[4.900]$	$[1.2635] - i[2.5424]$
2	$[4.879]$	$[2.0109] - i[4.0218]$
3	$[5.08]$	$[4.43]$
$\eta = 3/2.$		
1	$[1.35853] - i[2.74171]$	$[1.6160] - i[1.3389]$
2	$[2.100] - i[4.200]$	$[2.8566] - i[3.715]$
3	$[4.633]$	$[3.622] - i[5.243]$
4	$[6.09]$	$[4.16]$
$\eta = 9/4.$		
1	$[1.52056] - i[1.94164]$	$[1.69832] - i[1.72202]$
2	$[1.36224] - i[2.74060]$	$[1.58138] - i[1.24719]$
3	$[2.18132] - i[4.36275]$	$[2.77736] - i[3.55628]$
4	$[4.87043] - i[7.7391]$	$[3.6612] - i[5.322]$
5	$[5.377] - i[10.75]$	$[4.3277] - i[8.66]$
6	$[7.80] - i[13.6]$	$[6.88] - i[11.77]$
$\eta = 2.$		
1	$[1.68350] - i[1.80011]$	$[1.66493] - i[1.63580]$
2	$[2.98851] - i[3.98120]$	$[1.40882] - i[2.84950]$
3	$[3.78029] - i[5.46059]$	$[2.44577] - i[4.89188]$
4	$[4.32695] - i[8.654]$	$[3.23189] - i[6.4638]$
5	$[6.7764]$	$[5.8390]$
6	$[7.0937]$	$[6.2901]$
$\eta = 7/4.$		
1	$[1.63910] - i[1.40580]$	$[1.67342] - i[1.52299]$
2	$[2.67067] - i[3.14194]$	$[1.16474] - i[2.33907]$
3	$[3.22168] - i[6.44]$	$[2.06571] - i[4.1315]$
4	$[5.708]$	$[4.7389]$
5	$[6.042]$	$[5.228]$

For a systematic calculation it appears preferable to employ the forms (k) , (l) rather than the expansions in powers of μ . The functions involving P, once calculated for the various values of n , are then available for any value of η . The following table exhibits the algebraic forms:—

n .	$\frac{(2n+1)P'_n}{n(n+1)}$	$\frac{(2n+1)\mu P'_n}{n(n+1)} - (2n+1)P_n$
1	$\frac{3}{2}\mu$	$-\frac{3}{2}\mu$
2	$\frac{5}{2}\mu$	$-\frac{5}{2}\mu(1-2\mu^2)$
3	$\frac{7}{2}\mu(-1+5\mu^2)$	$-\frac{7}{2}\mu(11\mu-15\mu^3)$
4	$\frac{9}{2}\mu(-3\mu+7\mu^3)$	$-\frac{9}{2}\mu(-3+27\mu^2-28\mu^4)$
5	$\frac{11}{2}\mu(1-14\mu^2+21\mu^4)$	$-\frac{11}{2}\mu(-29\mu+126\mu^3-105\mu^5)$
6	$\frac{13}{2}\mu(5\mu-80\mu^3+33\mu^5)$	$-\frac{13}{2}\mu(5-100\mu^2+285\mu^4-198\mu^6)$

The particular cases $\mu = 0, \mu = \pm 1$ have already been considered. It will be observed that both functions are either entirely odd or entirely even.

The tables give the logarithmic values for $\mu = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$. Thus, in the first table for $\mu = \frac{1}{4}, n = 4$, we have the number whose logarithm is $\bar{1} \cdot 85776$, and this is to be taken negatively when $\mu = +\frac{1}{4}$. Moreover, since this function of μ is odd, the sign is to be reversed, *i.e.*, made positive, when $\mu = -\frac{1}{4}$.

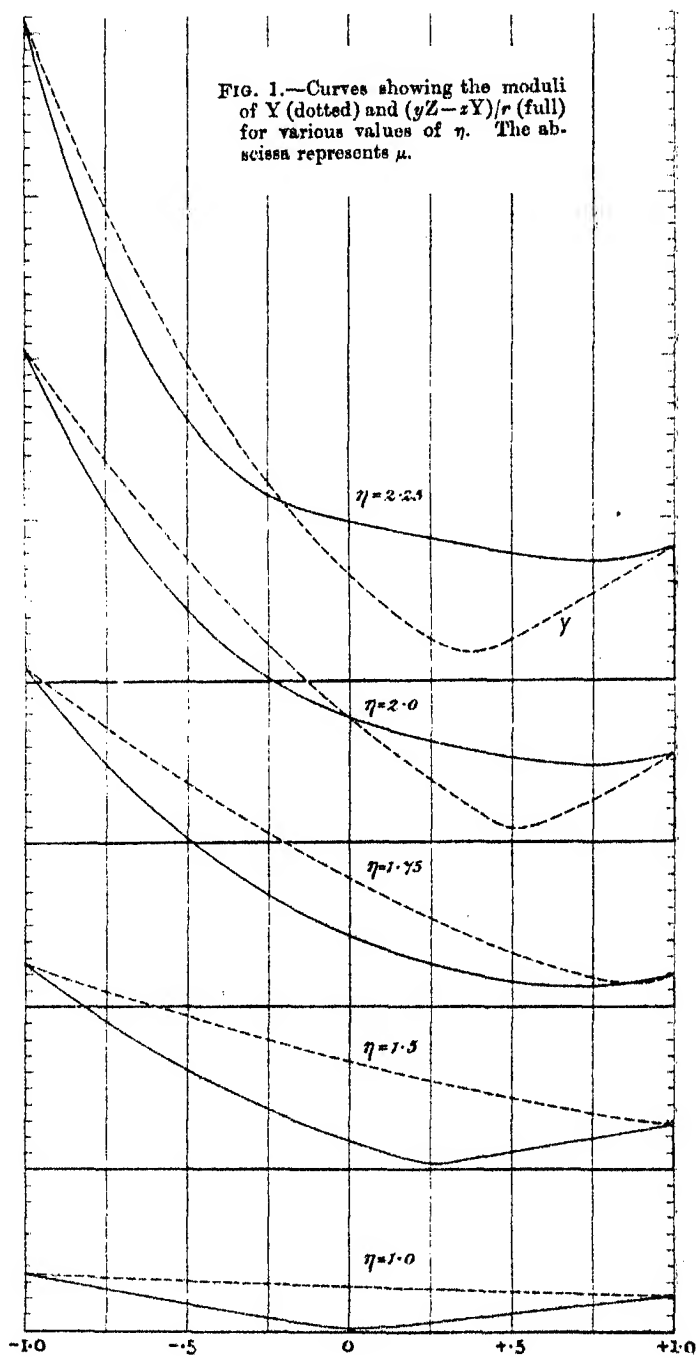
Table for $\frac{(2n+1)P'_n}{n(n+1)}$.

n .	$\mu = 0$.	$\mu = \frac{1}{4}$.	$\mu = \frac{1}{2}$.	$\mu = \frac{3}{4}$.	$\mu = 1$.
1	+ [0.17609]	+ [0.17609]	+ [0.17609]	+ [0.17609]	+ [0.17609]
2	0	+ [I.79588]	+ [0.09691]	+ [0.27300]	+ [0.39794]
3	- [I.94201]	- [I.77928]	+ [I.33995]	+ [0.20029]	+ [0.54407]
4	0	- [I.85776]	- [I.84703]	+ [I.89819]	+ [0.65321]
5	+ [I.83727]	+ [I.15331]	- [I.91191]	- [I.19988]	+ [0.74036]
6	0	+ [I.82016]	- [I.24977]	- [I.94131]	+ [0.81291]

Table for $\frac{\mu P'_n(2n+1)}{n(n+1)} - (2n+1)P_n$.

n .	$\mu = 0$.	$\mu = \frac{1}{4}$.	$\mu = \frac{1}{2}$.	$\mu = \frac{3}{4}$.	$\mu = 1$.
1	0	- [I.57403]	- [I.87506]	- [0.05115]	- [0.17609]
2	+ [0.39794]	+ [0.33995]	+ [0.09691]	- [I.49485]	- [0.39794]
3	0	+ [0.34285]	+ [0.50132]	+ [0.22573]	- [0.54407]
4	- [0.52827]	- [0.20401]	+ [0.35218]	+ [0.57335]	- [0.65321]
5	0	- [0.56836]	- [0.14504]	+ [0.64946]	- [0.74036]
6	+ [0.60879]	- [I.17713]	- [0.68256]	+ [0.47638]	- [0.81291]

The way is now clear for the last step, *viz.*, the calculation of $(yZ - zY)/r$ and Y by summation with respect to n of the values given in (l) and (k). As to this there is little to call for special remark. Of course the odd and even terms are added separately.



The tables exhibit the complex values and the modulus, subject to multiplication by the factor $(kr)^{-1}e^{ik(ct-r)}$. Thus for $\eta = 1$, $\mu = -1$, we have

$$\frac{yZ - zY}{r} = \frac{e^{ik(ct-r)}}{kr} (0.3457 - i \times 0.0538) = 0.3499 \frac{e^{ik(ct-r-\rho)}}{kr},$$

where ρ influences the phase only.

As regards the values of η , or kR , or $2\pi R/\lambda$, the numbers 1, $3/2$, $9/4$ were at first chosen. Subsequently it appeared desirable to fill up the gap at the more interesting stage, and so calculations for $\eta = 1\frac{1}{2}$, $\eta = 2$ were added. The values of the *modulus* are plotted in the curves, fig. 1, as functions of μ for the various values of η . It will be remembered that in all cases the refractive index is supposed to be 1.5.

μ .	$\frac{yZ - zY}{r}$.	Modulus.	Y.	Modulus.
$\eta = 1.$				
-1	0.3457 - i x 0.0538	0.3499	0.3457 - i x 0.0538	0.3499
$-\frac{3}{2}$	0.2525 - i x 0.0404	0.2557	0.3266 - i x 0.0534	0.3310
$-\frac{1}{2}$	0.1669 - i x 0.0272	0.1691	0.3083 - i x 0.0530	0.3128
$-\frac{1}{4}$	0.0884 - i x 0.0141	0.0895	0.2904 - i x 0.0527	0.2951
0	0.0165 - i x 0.0009	0.0165	0.2731 - i x 0.0523	0.2781
$+\frac{1}{4}$	-0.0490 + i x 0.0121	0.0505	0.2566 - i x 0.0519	0.2618
$+\frac{1}{2}$	-0.1083 + i x 0.0250	0.1111	0.2405 - i x 0.0516	0.2460
$+\frac{3}{4}$	-0.1619 + i x 0.0380	0.1663	0.2250 - i x 0.0512	0.2307
+1	-0.2103 + i x 0.0508	0.2164	0.2103 - i x 0.0508	0.2164
$\eta = 1.5.$				
-1	1.1902 - i x 0.4237	1.2634	1.1902 - i x 0.4237	1.2034
$-\frac{3}{2}$	0.8463 - i x 0.3302	0.9084	1.0212 - i x 0.3992	1.0965
$-\frac{1}{2}$	0.5647 - i x 0.2401	0.6136	0.8643 - i x 0.3751	0.9422
$-\frac{1}{4}$	0.3388 - i x 0.1533	0.3719	0.7190 - i x 0.3510	0.8001
0	0.1629 - i x 0.0698	0.1772	0.5844 - i x 0.3270	0.6697
$+\frac{1}{4}$	0.0316 + i x 0.0103	0.0333	0.4602 - i x 0.3032	0.5511
$+\frac{1}{2}$	-0.0597 + i x 0.0875	0.1059	0.3453 - i x 0.2793	0.4441
$+\frac{3}{4}$	-0.1159 + i x 0.1614	0.1987	0.2390 - i x 0.2556	0.3499
+1	-0.1414 + i x 0.2321	0.2718	0.1414 - i x 0.2321	0.2718
$\eta = 1.75.$				
-1	1.8683 - i x 0.9404	2.0917	1.8683 - i x 0.9404	2.0917
$-\frac{3}{2}$	1.2802 - i x 0.7661	1.4919	1.4992 - i x 0.8280	1.7127
$-\frac{1}{2}$	0.8380 - i x 0.6059	1.0301	1.1668 - i x 0.7165	1.3693
$-\frac{1}{4}$	0.5081 - i x 0.4597	0.6852	0.8694 - i x 0.6060	1.0598
0	0.2386 - i x 0.3273	0.4363	0.6041 - i x 0.4964	0.7819
$+\frac{1}{4}$	0.1592 - i x 0.2085	0.2623	0.3682 - i x 0.3878	0.5347
$+\frac{1}{2}$	0.1067 - i x 0.1032	0.1484	0.1594 - i x 0.2801	0.3223
$+\frac{3}{4}$	0.1191 - i x 0.0112	0.1196	-0.0251 - i x 0.1734	0.1752
+1	0.1858 + i x 0.0675	0.1977	-0.1858 - i x 0.0675	0.1977

μ .	$\frac{yZ - zY}{r}$.	Modulus.	Y.	Modulus.
$\eta = 2.$				
-1	$2.4767 - i \times 1.7984$	3.0608	$2.4767 - i \times 1.7984$	3.0608
$-\frac{3}{4}$	$1.4988 - i \times 1.4716$	2.1005	$1.8327 - i \times 1.4949$	2.3650
$-\frac{1}{2}$	$0.8053 - i \times 1.1919$	1.4384	$1.2909 - i \times 1.1980$	1.7611
$-\frac{1}{4}$	$0.8478 - i \times 0.9583$	1.0195	$0.8417 - i \times 0.9076$	1.2379
0	$0.0639 - i \times 0.7699$	0.7745	$0.4759 - i \times 0.6235$	0.7844
$+\frac{1}{4}$	$-0.0228 - i \times 0.6257$	0.6261	$0.1855 - i \times 0.3459$	0.3925
$+\frac{1}{2}$	$-0.0040 - i \times 0.5247$	0.5247	$-0.0872 - i \times 0.0747$	0.0824
$+\frac{3}{4}$	$+0.1132 - i \times 0.4680$	0.4705	$-0.1988 + i \times 0.1901$	0.2751
+1	$+0.8056 - i \times 0.4487$	0.5429	$-0.3056 + i \times 0.4487$	0.5429
$\eta = 2.25.$				
-1	$3.0635 - i \times 2.0979$	4.0822	$3.0635 - i \times 2.0979$	4.0822
$-\frac{3}{4}$	$1.5157 - i \times 2.0593$	2.5569	$1.9791 - i \times 2.1286$	2.9065
$-\frac{1}{2}$	$0.4857 - i \times 1.5448$	1.6193	$1.1464 - i \times 1.5972$	1.9661
$-\frac{1}{4}$	$-0.1392 - i \times 1.1497$	1.1581	$0.5364 - i \times 1.1036$	1.2270
0	$-0.4540 - i \times 0.8696$	0.9810	$0.1234 - i \times 0.6473$	0.6590
$+\frac{1}{4}$	$-0.5383 - i \times 0.6999$	0.8830	$-0.1157 - i \times 0.2281$	0.2558
$+\frac{1}{2}$	$-0.4585 - i \times 0.6364$	0.7844	$-0.2018 + i \times 0.1544$	0.2541
$+\frac{3}{4}$	$-0.2689 - i \times 0.6745$	0.7261	$-0.1531 + i \times 0.5003$	0.5232
+1	$-0.0139 - i \times 0.8101$	0.8102	$+0.0139 + i \times 0.8101$	0.8102

When $\eta = 1$, *i.e.*, when the circumference of the sphere equals the wavelength in the general medium, there is comparatively little departure from the conditions appropriate to the infinitely small sphere. When the secondary ray is in a direction perpendicular to that of primary vibration, *viz.*, when $y = 0$, the vibration (Y) varies but little with μ . It is otherwise when the secondary ray is in the plane containing the directions of the primary ray and of primary vibration. The second column shows that in that case the secondary vibration varies greatly with μ , and that in the perpendicular direction ($\mu = 0$) the intensity is very small. This is the direction in which there would be no effect, however large the sphere, if the square of the difference of optical quality could be neglected absolutely.

The departure from the law of the infinitely small sphere becomes more apparent when $\eta = 1.5$. The principal feature here is the displacement of the maximum polarisation from $\mu = 0$ to the neighbourhood of $\mu = +\frac{1}{4}$, *i.e.*, to a direction inclining *backwards* along the course of the incident light. When the incident light is unpolarised, the diffracted light is polarised at all angles (other than $\mu = \pm 1$), and in the same sense as from infinitely small particles.

The latter law ceases to hold when η rises to about 1.75. A third neutral point (direction of no polarisation) enters at $\mu = +1$ and moves inwards.

When $\eta = 2$, the change has proceeded so far that the neutral point is in the neighbourhood of $\mu = 0$, the polarisation for positive μ being the *reverse* of that found for infinitely small particles. At $\mu = +\frac{1}{2}$ the reversed polarisation is very pronounced. When η attains 2.25, the neutral point is still further on (near $\mu = -\frac{1}{2}$), and the maximum reverse polarisation is near $\mu = \frac{1}{2}$. It will be seen that these changes occur very rapidly in the neighbourhood of $\eta = 2$.

It would be possible to follow these calculations to greater values of η , and such an extension would not be without interest, but the arithmetical work would soon become heavy. Also, without increasing η , the refractive index might be varied. Some data for such calculations are included in the tables already given.

So far the primary light has been supposed to be either unpolarised, or, if polarised, to be plane polarised in one or other principal plane. In the more general case recourse must be had to the complex expressions, which allow the effects of the two principal components of the primary light to be combined, with the necessary allowance for any phase-difference. But it is scarcely necessary to pursue the treatment of this part of the subject.

Experimental.

So far as I know, the only experimental work bearing at all closely upon the preceding calculations is that of Govi and Tyndall ('Proc. Roy. Soc.,' January, 1869), who observed the light scattered from smoke of various kinds. Tyndall established the existence of neutral points at angles dependent upon the condition of the smoke, but his indications are not very precise. For example, he does not distinguish between density due to increased number of particles in a given space and that due to increasing size, of which the effects may be expected to be very different. Nor, again, do I see any suggestion that the position of the neutral point varies with the colour of the light. Nevertheless, Tyndall's description is suggestive, and it formed the starting-point of my own work upon the subject.

In continuation of the experiments already referred to at the commencement of this paper, I have lately repeated the observation on the nascent precipitate formed when a little acid is added to a dilute and well-filtered solution of hyposulphite. The liquid was contained in a small beaker placed in a dark room and exposed to a beam of sunlight. The observation of the light dispersed at various angles may be made with a nicol, but a double image prism is better. This may be mounted at one end of a tube of which the other carries a small aperture of such dimensions that two oppositely polarised rectangular fields are seen in close juxtaposition. In the early

stage the double-image prism, suitably rotated, shows complete polarisation of the light scattered along BC, fig. 2, at right angles to the primary rays AB. Somewhat later the minimum light seen along BC shows Tyndall's "residual

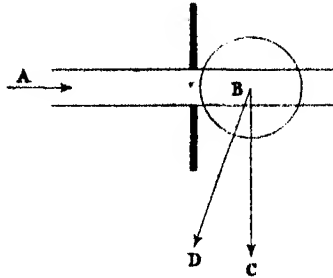


FIG. 2.

blue," indicating that for this colour the polarisation is no longer complete. But if the direction of observation be changed towards BD, the polarisation is improved. As the particles grow, a stage is reached in which the effects for blue and red light are well contrasted. If a blue glass be inserted in the course either of the primary or of the secondary light, that polarised component which originally vanished (along BC) is found along BD to be the brighter of the two, showing that the polarisation is *reversed*. The substitution of a red for the blue glass restores the original character of the polarisation, the increase in the wave-length compensating the growth of the particles. It is not pretended that the observed contrast is as great as the theoretical curves might suggest; nor could this reasonably be expected, seeing that the particles are not all of the same size.

April 30.—I have recently learned from Prof. Love that he had become aware of the error in equation XVIII, and that a correction was published in "Math. Soc. Proc.," vol. 31, p. 489.

On the Improbability of a Random Distribution of the Stars in Space.

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(1) The object of the present paper is to discuss certain statistical distributions of the stars, and to consider how far they are in accordance with our experience so far as that extends. For direct tests we require far more numerous determinations of parallax than are at present available.

The largest sample of parallaxes hitherto published is that due to Kapteyn,* but, for reasons elsewhere stated, I do not feel able to include this in my survey. Small series collected by Newcomb and determined by the Yale observers will be considered below.

The main point of my investigation will, however, turn on certain parallax constants, which frequently arise in stellar statistical investigations, and which are capable of determination without a knowledge of absolute parallax.

I shall use the following notation: m = a stellar magnitude, D = an absolute stellar distance, $\pi = c/D$ = a stellar parallax,† c being a constant, depending on the unit of measurement and the diameter of the earth's orbit. $P = \log_{10} \pi = \log_{10} c - \log_{10} D$, is the logarithm of the parallax. A rule over any of these quantities will denote their mean values. σ_m , σ_D , σ , σ_P will represent their standard deviations, or square roots of mean square deviations from the mean values.

V will denote what is termed a coefficient of variation, or the ratio of a standard deviation to the corresponding mean value.

$V_D = \sigma_D/\bar{D}$, $V_\pi = \sigma_\pi/\bar{\pi}$, and σ_P are the parallax constants which naturally arise in the course of stellar statistics, and which to some extent can be measured without the aid of absolute parallax determinations.

The letter r will be used throughout for a correlation coefficient, the attached subscripts denoting the characteristic whose association is under discussion.

(2) Let L_1 represent the light of a star; then this light depends: (a) on the size of the star; (b) its intrinsic brightness; (c) its distance from us; and,

* "The Parallaxes of 3650 Stars of different Galactic Latitudes," J. C. Kapteyn and W. de Sitter, 'Publications of the Astronomical Laboratory at Groningen,' No. 20, 1908.

† I have retained π for parallax in accordance with much astronomical usage, although it introduces some confusion when $\pi = 3.14...$ occurs in the same equations, and still more if it appears in the form $\sin \pi$. p and P are needed for many other purposes. In manuscript I invariably write Π , but this never meets with the printer's approval.

possibly (d), on the existence of interstellar absorption. Or, if λ represent an absorption coefficient, we shall have

$$L_1 = \frac{F_1}{D_1^2} 10^{-\lambda D_1},$$

or, $\log_{10} L_1 = \log_{10} F_1 - 2 \log_{10} D_1 - \lambda D_1$, where F_1 depends solely on the constitution of the star.

But if we measure light in terms of the stellace, *i.e.*, the light, L_0 , of a star of tenth-magnitude as unit, and use Pogson's value of the constant, we have

$$\log_{10} L_1 = 4 - 0.4 m_1 + \log_{10} L_0,$$

and transferring to parallax,

$$4 - 0.4 m_1 = \log_{10} F_1 - \log_{10} L_0 - 2 \log_{10} c + 2 \log_{10} \pi - \lambda c / \pi,$$

or

$$m_1 = f_1 - 5 \log_{10} \pi + 2.5 \lambda c / \pi.$$

Here f_1 is entirely independent of the star's parallax; it contains a constant, $10 + 2.5 \log_{10} L_0 + 5 \log_{10} c$, which disappears when we consider deviations from mean values, and a quantity, $2.5 \log_{10} F_1$, which depends solely on the intrinsic brightness and size of the star. With our present knowledge there is no reason whatever for supposing any association between the distance of a star from the sun and its size or intrinsic brightness. We shall therefore suppose $r_{\pi f} = 0$. Further, if there be an absorption term, we may suppose it so small that for our first approximation we can put $\lambda = 0$. Thus we write:

$$m_1 = f_1 - 5 P_1,$$

whence it follows that for any series of stars

$$\bar{m}_1 = \bar{f}_1 - 5 \bar{P}_1,$$

$$\sigma_{m_1}^2 = \sigma_{f_1}^2 + 25 \sigma_{P_1}^2.$$

It is accordingly clear that for any system of stars, the easily calculable σ_{m_1} must be greater than the value $5 \sigma_{P_1}$ obtained from any suggested theoretical distribution. We thus have a means of testing the possible non-applicability of various theoretical systems.

Again, let there be a second magnitude, m_2 , arising from a light phenomenon at the same or sensibly the same distance from us as m_1 . This can arise in the cases of variable stars and of double stars. Then we have

$$m_2 = f_2 - 5 P_1,$$

$$\bar{m}_2 = \bar{f}_2 - 5 \bar{P}_1,$$

$$\sigma_{m_2}^2 = \sigma_{f_2}^2 + 25 \sigma_{P_1}^2.$$

Whence, if N be the number of stars dealt with,

$$\frac{S(m_1 - \bar{m}_1)(m_2 - \bar{m}_2)}{N} = \frac{S(f_1 - \bar{f}_1)(f_2 - \bar{f}_2)}{N} + 25 \frac{S(P - \bar{P})^2}{N},$$

i.e.,

$$\sigma_{m_1} \sigma_{m_2} r_{m_1 m_2} = \sigma_{f_1} \sigma_{f_2} r_{f_1 f_2} + 25 \sigma_P^2.$$

Thus, if there be no association between the actual lights emitted, we should have

$$\sigma_{m_1} \sigma_{m_2} r_{m_1 m_2} = 25 \sigma_P^2,$$

the left-hand side of which is determinable for any series by observation and calculation. This provides another method of ascertaining whether a theoretical distribution is applicable in the case of light phenomena at the same distance which are assumed to be independent.

In general

$$r_{f_1 f_2} = \frac{\sigma_{m_1} \sigma_{m_2} r_{m_1 m_2} - 25 \sigma_P^2}{\sqrt{\sigma_{m_1}^2 - 25 \sigma_P^2} \sqrt{\sigma_{m_2}^2 - 25 \sigma_P^2}},$$

which enables us to ascertain the actual relationship between light-giving capacities, if we can hypothesise a reasonable distribution for the stars under discussion. Thus, for example, we might, perhaps, assume to a first approximation that double stars are scattered at random in space, and might inquire whether any relationship exists between the intrinsic brilliancies of the primary and secondary.

(3) My proposed discussion will naturally break up into two parts. First, the consideration of what values these parallax constants take for theoretical stellar distributions; and secondly, how far any system of stars observable by us, and for that very reason a selected system, is likely to be a random sample of such theoretical systems.

I consider first some sample theoretical distributions.

(4) Both Newcomb and Pickering have investigated in the first place the effect on parallax frequencies of the uniform distribution of stars through space. This appears an obviously reasonable suggestion, although, as we advance, weighty reasons will arise for modifying this standpoint. I take first:—

The Values of V_D , V_π , and σ_P for a Uniform Distribution of the Stars throughout a Sphere of radius b .

Let ρ be the density of the stars per unit volume, then

$$\frac{4}{3} \pi b^3 \rho \bar{D} = \int_0^b 4 \pi r^2 \rho r dr, \quad \text{or} \quad \bar{D} = \frac{3}{4} b,$$

$$\frac{4}{3} \pi b^3 \rho \sigma_D^2 = \int_0^b 4 \pi r^2 \rho (r - \frac{3}{4} b)^2 dr, \quad \text{or} \quad \sigma_D^2 = \frac{3}{8} b^2.$$

Hence

$$V_D = \sqrt{\frac{3}{16}} = 0.258.$$

Again

$$\frac{4}{3} \pi b^3 \rho \pi = \int_0^b 4 \pi r^2 \rho \frac{c}{r} dr, \quad \text{or} \quad \pi = \frac{3}{2} \frac{c}{b},$$

$$\frac{4}{3} \pi b^3 \rho \sigma_\pi^2 = \int_0^b 4 \pi r^2 \rho \left(\frac{c}{r} - \frac{3}{2} \frac{c}{b} \right)^2 dr, \quad \text{or} \quad \sigma_\pi^2 = \frac{3}{4} \left(\frac{c}{b} \right)^2.$$

Hence

$$V_{\pi} = \sqrt{\frac{1}{3}} = 0.577.$$

Lastly, if μ be the modulus = 0.43429,

$$\frac{4}{3}\pi b^3 \rho \bar{P} = \int_0^b 4\pi r^2 \rho \mu \log_e \frac{c}{r} dr,$$

and, integrating by parts,
$$= \frac{4}{3}\pi b^3 \mu \log_e \frac{c}{b} + \frac{4\pi b^3}{9} \mu,$$

or

$$\bar{P} = \mu \left(\log_e \frac{c}{b} + \frac{1}{3} \right).$$

Again

$$\begin{aligned} P - \bar{P} &= \mu \left(\log_e \frac{c}{r} - \log_e \frac{c}{b} - \frac{1}{3} \right) \\ &= \mu (k - \log_e r), \end{aligned}$$

where $k = \log_e b - \frac{1}{3}$. Thus we have

$$\frac{4}{3}\pi b^3 \rho \sigma_P^2 = \int_0^b 4\pi r^2 \rho \mu^2 (k - \log_e r)^2 dr = \int_0^b 4\pi \mu^2 (\log_e r)^2 d\left(\frac{1}{3}r^3\right) - \mu^2 k^2 \frac{4\pi b^3}{3}.$$

Hence, integrating twice by parts and evaluating the indeterminate terms, we find

$$\frac{4}{3}\pi b^3 \rho \sigma_P^2 = \frac{4}{3}\pi b^3 \mu^2 [(\log_e b)^2 - \frac{2}{3} \log_e b + \frac{2}{9} - k^2],$$

or

$$\sigma_P^2 = \frac{1}{9}\mu^2, \quad \sigma_P = \frac{1}{3}\mu = 0.1448.$$

The special quantity generally needed, $25\sigma_P^2$, is given by

$$25\sigma_P^2 = 2.778 \mu^2 = 0.5240.$$

Now the results reached are, supposing the stars dealt with to be uniformly distributed throughout space, of some interest. We see that they are quite independent of the radius b over which we extend the sphere of our observations. Further, we remark that $\sigma_{m_1}^2$, $\sigma_{m_2}^2$, and $\sigma_{m_1 m_2}$ ought in all cases where we may reasonably assume a uniform distribution to come out greater than 0.524.

(5) I will now proceed to modify these constants by supposing the stellar universe arranged in two spherical layers about the sun, each layer having uniform but individual density. Let δ_1 be the density up to radius b_1 , and δ_2 the density from b_1 to b_2 . Then it follows that

$$V_D = 0.258 \left\{ 1 + \frac{16(b_1 - b_2)^2 b_1^3 b_2^3 \delta_2 (\delta_1 - \delta_2)}{(b_1^4 (\delta_1 - \delta_2) + b_2^4 \delta_2)^2} \right\}^{\frac{1}{2}},$$

$$V_{\pi} = 0.577 \left\{ 1 + \frac{4(b_1 - b_2)^2 b_1 b_2 \delta_2 (\delta_1 - \delta_2)}{(b_1^3 (\delta_1 - \delta_2) + b_2^3 \delta_2)^2} \right\}^{\frac{1}{2}},$$

and
$$25\sigma_P^2 = 0.5240 + \frac{25 b_1^3 b_2^3 \delta_2 (\delta_1 - \delta_2) (\log_{10} b_2 / b_1)^2}{(b_1^3 (\delta_1 - \delta_2) + b_2^3 \delta_2)^2}.$$

It is clear that to raise the values of V_D , V_{π} , and $25\sigma_P^2$, we must make δ_2 less than δ_1 . In other words, in a general way these parallax constants will

be higher if the stellar universe is rarer at greater distances from us. But the changes are not very rapid. If we make $b_2 = 2b_1$, then for $\delta_1 = 2\delta_2$, we find $25\sigma_P^2$ only 0.748, and for $\delta_1 = 9\delta_2$, a very improbable supposition, $25\sigma_P^2$ has only risen to 1.090. For $b_2 = 4b_1$, the values for the same densities are 0.661 and 1.419.

A dense nucleus round the sun appears the only way in which substantial change could be made in these parallax constants.

(6) I do not stay to discuss these points, because another method of investigating the problem will throw light on other matters also. If we supposed our stellar universe to be spheroidal in form, or that we dealt with a spheroidal portion of it, we should clearly be approaching the same result, after a certain limit, as supposing the density to decrease with the distance from the sun.

We need not reject such a system with the sun in the centre as necessarily idle, for we are only considering the nature of the changes which very rough approximations to the actual state of affairs will make in the parallax constants.

In particular, the limit to the oblate spheroid may be looked upon as a flat stellar universe, and this "buulike" universe is worth consideration. Again, the limit to a prolate spheroid is a columnar universe, and, the constants of such a columnar universe being determined, we can superpose two such columnar universes, and obtain the parallax constants for a double drift system.

The polar axis of our spheroid being $2b$ and the equatorial axis $2a$, I find for the mean distance of the population from its centre

$$\bar{D} = \frac{2}{3}b \left\{ 1 + \frac{1+\eta^2}{\eta} \tan^{-1}\eta \right\} = \frac{2}{3}a \left\{ \frac{1}{(1+\eta^2)^{\frac{1}{2}}} + \frac{(1+\eta^2)^{\frac{1}{2}}}{\eta} \tan^{-1}\eta \right\},$$

where $\eta = (a^2/b^2 - 1)^{\frac{1}{2}}$, for the oblate spheroid; and

$$\bar{D} = \frac{2}{3}b \left\{ 1 + \frac{1-\epsilon^2}{\epsilon} \log_e \sqrt{\frac{1+\epsilon}{1-\epsilon}} \right\},$$

where $\epsilon = (1 - a^2/b^2)^{\frac{1}{2}}$, for the prolate spheroid. Further

$$\sigma_D = \sqrt{\frac{1}{3}(2a^2 + b^2) - \bar{D}^2}$$

for both. Hence $V_D = \sigma_D/\bar{D}$, can readily be found.

In the case of the parallax we have for the oblate spheroid

$$\pi = \frac{3c}{2b} \frac{\tan^{-1}\eta}{\eta},$$

$$V_\pi = \sqrt{\frac{4}{3} \frac{\sin \chi}{\chi^2} \log_e \cot \left(\frac{\pi}{4} - \frac{1}{2} \chi \right) - 1},$$

where $\cos \chi = b/a$ and $\eta = \tan \chi$.

For the prolate spheroid

$$\pi = \frac{3}{2} \frac{c}{b} \frac{1}{\epsilon} \log_e \sqrt{\frac{1+\epsilon}{1-\epsilon}},$$

$$V_\pi = \sqrt{\frac{4}{3} \frac{\psi \tan \psi}{\{\log_e \cot(\frac{1}{4}\pi - \frac{1}{2}\psi)\}^2 - 1}},$$

where $\cos \psi = a/b$ and $\epsilon = \sin \psi$.

These equations have been found by straightforward but somewhat laborious integration. The determinations of the mean, \bar{P} , and standard deviation, σ_P , of the parallax logarithm are not so simple.

We have

$$\begin{aligned} \frac{4}{3} \pi a^2 b \rho \bar{P} / \mu &= 2 \int_0^{\frac{1}{2}\pi} \int_0^r \rho 2\pi r \cos \theta r d\theta dr \log_e \frac{c}{r} \\ &= 4\pi \int_0^{\frac{1}{2}\pi} \int_0^r \rho \log_e \frac{c}{r} d\left(\frac{1}{3} r^3\right) d\sin \theta, \\ &= \frac{4\pi}{3} \int_0^{\frac{1}{2}\pi} \rho \left(r^3 \log_e \frac{c}{r} + \frac{1}{3} r^3\right) d\sin \theta. \end{aligned}$$

Let $r = av$, then $v^2 = (1 + \eta^2 \sin^2 \theta)^{-1}$ for the oblate spheroid, and $\sin \theta = \eta^{-1} \sqrt{1/v^2 - 1}$. Change the integration to v , and we have

$$\bar{P} = \frac{\mu a}{b\eta} \int_1^{b/a} \left(\log_e \frac{c}{av} + \frac{1}{3} \right) d\sqrt{1-v^2} = \mu \left(\frac{1}{3} + \log_e \frac{c}{b} + \gamma \right),$$

on integrating by parts, where

$$\gamma = 1 - \frac{\sqrt{1+\eta^2}}{\eta} \log_e (\eta + \sqrt{1+\eta^2}),$$

and vanishes when $\eta = 0$. Next,

$$\begin{aligned} \frac{4}{3} \pi a^2 b \rho \sigma_P^2 &= 2 \int_0^{\frac{1}{2}\pi} \int_0^r \rho 2\pi r \cos \theta r d\theta dr \left(\mu \log_e \frac{c}{r} - \bar{P} \right)^2, \\ &= \frac{4}{3} \pi \rho \mu^2 \int_0^{\frac{1}{2}\pi} \int_0^r d(\sin \theta) d(r^3) \left(\log_e \frac{c}{r} - \nu \right)^2, \end{aligned}$$

where $\nu = \frac{1}{3} + \gamma$. Whence

$$\begin{aligned} \frac{4}{3} \pi a^2 b \rho \sigma_P^2 &= \frac{4\pi\rho}{3} \mu^2 \int_0^{\frac{1}{2}\pi} \int_0^r d(\sin \theta) d(r^3) \left(\log_e^2 \frac{b}{r} - \nu^2 \right) \\ &= \frac{4\pi\rho}{3} \mu^2 \int_0^{\frac{1}{2}\pi} d(\sin \theta) \left(r^3 \log_e^2 \frac{b}{r} + \frac{2r^3}{3} \log_e \frac{b}{r} + \frac{2}{3} r^3 - \nu^2 r^3 \right). \end{aligned}$$

Put $r = av$ again, and change to an integration with regard to v . We find

$$\sigma_P^2 = \frac{a\mu^2}{b\eta} \int_1^{b/a} \left(\log_e^2 \frac{b}{av} + \frac{2}{3} \log_e \frac{b}{av} + \frac{2}{3} - \nu^2 \right) d\sqrt{1-v^2}.$$

Integrating by parts, the first term will be found to vanish between the limits, and we have

$$\sigma_P^2/\mu^2 = \frac{2a}{b\eta} \int_1^{b/a} \log_e \frac{b}{av} \frac{\sqrt{1-v^2}}{v} dv + \frac{2}{3}\gamma + \frac{2}{9} + (\frac{1}{3} + \gamma)^2,$$

or $\sigma_P^2/\mu^2 = \frac{1}{3} - \gamma^2 + I,$

where I is the integral. It will be found that

$$I = -\gamma \log_e(1+\eta^2) - \frac{2a}{b\eta} \int_{b/a}^1 \frac{\sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv,$$

or
$$25\sigma_P^2/\mu^2 = 2.778 - 25\gamma^2 - 25\gamma \log_e(1+\eta^2) - \frac{50\sqrt{1+\eta^2}}{\eta} \int_{b/a}^1 \frac{\sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv.$$

To find the last integral we put

$$\begin{aligned} \int_{b/a}^1 \frac{\sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv &= \int_{b/a}^1 \frac{1}{v} \log_e \frac{1}{v} dv - \int_{b/a}^1 \frac{1-\sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv \\ &= \frac{1}{2} \left(\log_e \frac{a}{b} \right)^2 - \int_{b/a}^1 \frac{1-\sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv. \end{aligned}$$

The latter integral is finite from 0 to 1. The curve given by

$$z = \frac{1-\sqrt{1-v^2}}{v} \log_e \frac{1}{v}$$

was plotted for the range 0 to 1 and mechanically integrated.

For the prolate spheroid by a similar process we have

$$P = \mu \left(\frac{1}{3} - \log_e \frac{c}{b} - \gamma' \right),$$

where $\gamma' = 1 - \frac{\sqrt{1-\epsilon^2}}{\epsilon} \sin^{-1} \epsilon,$

and $\sigma_P^2/\mu^2 = \frac{1}{3} - \gamma'^2 - \gamma' \log_e(1-\epsilon^2) - \frac{2\sqrt{1-\epsilon^2}}{\epsilon} \int_1^{b/a} \frac{\sqrt{v^2-1}}{v} \log_e v dv,$

or

$$25\sigma_P^2/\mu^2 = 2.778 - 25\gamma'^2 - 25\gamma' \log_e(1-\epsilon^2) - \frac{50\sqrt{1-\epsilon^2}}{\epsilon} \int_1^{b/a} \frac{\sqrt{v^2-1}}{v} \log_e v dv.$$

To find the integral, I take

$$\begin{aligned} \int_1^{b/a} \frac{\sqrt{v^2-1}}{v} \log_e v dv &= \int_1^{b/a} \log_e v dv - \int_1^{b/a} \frac{v-\sqrt{v^2-1}}{v} \log_e v dv \\ &= \frac{b}{a} \left(\log_e \frac{b}{a} - 1 + \frac{a}{b} \right) - \int_1^{b/a} \frac{v-\sqrt{v^2-1}}{v} \log_e v dv. \end{aligned}$$

The subject of the latter integral always remains finite. The curve $z = \frac{v-\sqrt{v^2-1}}{v} \log_e v$ was plotted and mechanically integrated up to the values required.

The following table gives the chief stages in the determination of $25\sigma_P^2$:—

Oblate Spheroid.

Ratio of axes.	γ .	$\frac{1}{2} \left(\log_e \frac{a}{b} \right)^2$.	$\int_{b/a}^1 \frac{1 - \sqrt{1-v^2}}{v} \log_e \frac{1}{v} dv$.
$a/b = 1000$	-6.6010	23.85854	0.13572
$a/b = 100$	-4.2986	10.60380	0.13559
$a/b = 10$	-2.0083	2.65095	0.12877
$a/b = 3$	-0.8697	0.60347	0.09098
$a/b = 2$	-0.5207	0.24023	0.05937

Prolate Spheroid.

Ratio of axes.	γ .	$\frac{b}{a} \left(\log_e \frac{b}{a} - 1 + \frac{a}{b} \right)$.	$\int_1^{b/a} \frac{\sqrt{v^2-1}}{v} \log_e v dv$.
$b/a = 2$	+0.3954	0.38029	0.08902
$b/a = 3$	+0.5648	1.29584	0.16606
$b/a = 10$	+0.8522	14.02585	0.35055
$b/a = 100$	+0.9844	361.51702	0.48890
$b/a = 1000$	+0.9984	5908.75528	0.59240

Substituting in the above equations, we obtain, after some arithmetic, the values of V_D , V_n , and $25\sigma_P^2$.

The following table results:—

	Ratio of axes.	V_n .	V_D .	$25\sigma_P^2$.
Oblate spheroid.	$a/b = \infty$	∞	0.391	1.360*
	$a/b = 1000$	1.771	0.391	1.360
	$a/b = 100$	1.378	0.391	1.354
	$a/b = 10$	0.914	0.385	1.210
	$a/b = 3$	0.680	0.343	0.842
	$a/b = 2$	0.622	0.309	0.680
	$a/b = 1$	0.577	0.258	0.524
Prolate spheroid.	$b/a = 2$	0.028	0.369	0.753
	$b/a = 3$	0.703	0.438	1.104
	$b/a = 10$	1.085	0.606	2.643
	$b/a = 100$	2.532	0.649	4.657
	$b/a = 1000$	6.046	0.650	5.148
	$b/a = \infty$	∞	0.650	5.239†

The limiting value of γ is $1 - \log_e 2 - \log_e \eta$, and again of

$$\sigma_P^2/\mu^2 = 2.778 - 25(1 - \log_e 2)^2 + 50 \times 0.13572.$$

The limiting value of ϵ is 1 and of γ' is $1/\epsilon$, and again of

$$\sigma_P^2/\mu^2 = 2.778 - 25(1 + \log_e(1 - \epsilon^2)) - 50 \left(\log_e \frac{b}{a} - 1 \right) = 27.778.$$

I shall speak of 0.524 as the "normal" value of the constant of the stellar system, $25\sigma_P^2$, since it is the value it would take if the stars were distributed at random through space. It is clear that to suppose the distribution spheroidal and not spherical will allow of some increase from the normal value, but far less for the "bunlike" than the columnar universe. It is desirable at this stage to compare these numbers with actual data, however slender.

(7) Kapteyn's parallax determinations being excluded, I can only give results deduced from the 72 stars cited by Newcomb* as having the best determined parallaxes, and from 163 stars observed at Yale.† The zero and negative parallaxes must of necessity be excluded, because they lead to infinite distance D and infinite logarithm of parallax P . This reduced for V_D and $25\sigma_P^2$ the number of stars to 69 Newcomb and 122 Yale—admittedly most slender and imperfect material.

We have, after some considerable arithmetic,

	V_D	V_π	$25\sigma_P^2$
Normal system	0.258	0.577	0.5240
Newcomb stars	1.075	0.924	4.212
Yale stars	1.017	1.443	3.111

For V_π I have, to see what effect it would produce, included the zero-parallax stars. The result is to separate more markedly the Newcomb and Yale series, and this was to be expected. For Newcomb excluded all but the best determined parallaxes, and so, many zero cases which would certainly be included by the Yale observers. For V_D the Newcomb and Yale stars give singularly accordant results, but wholly out of accord with the "normal" system. Nor is this to be wondered at. Parallax is subject to a very large error of observation, and our apparent σ_D and σ_π have not their true values, but values equal to $\sqrt{\sigma_D^2 + \sigma_{E_1}^2}$ and $\sqrt{\sigma_\pi^2 + \sigma_{E_2}^2}$, where σ_{E_1} and σ_{E_2} measure the variability in observational error in distance and parallax respectively. Now let us take $\sigma_{E_1} = \sigma_D$ and $\sigma_{E_2} = \sigma_\pi$, i.e. assume the variability in error to be as great as the quantity to be determined. This cannot be true, because to admit it is to assert that parallax determinations are wholly unreliable, but it will serve to indicate that the maximum limit to error does not suffice to reduce our observations to the "normal" values.

Dividing our apparent values by $\sqrt{2}$ we find $V_D = 0.760$ and 0.719

* 'The Stars: a Study of the Universe,' 1902.

† Chase, Smith, and Elkins, "Parallax Observations on 163 Stars," 'Trans. Yale Univ. Observ.,' vol. 2, pp. 1—207.

$V_{\pi}^* = 0.653$ and 1.020 for the Newcomb and Yale stars respectively. The reduction is considerable, but it will not bring the observations into accord with the extreme values of V_D for our spheroidal universe, still less with the theoretical "normal" values of $V_D = 0.258$, and $V_{\pi} = 0.577$. The theoretical and observed values for $25\sigma_P^2$ are still further out of agreement.

It must be at once admitted that the argument against a uniform distribution of the stars, based on these data, is not of much weight unless as confirming other results. In the first place we must suppose that we take a random sample of all the stars within a given distance (b) of the sun, *i.e.* with greater than a given parallax. In both cases the stars have been selected because they had big proper motions. Newcomb's stars have been largely chosen because they had a parallax greater than 0.00 , *i.e.* parallaxes only sensible in the third place of figures have been rejected, but we cannot assert that they are a random sample of all stars within a given sphere. Still the general agreement in V_D between the two independent series when we cut off all the zero (*i.e.* 0.00) parallaxes is remarkable, and carries some if not very great weight.

Returning now to our fundamental equation

$$\sigma_m^2 = \sigma_f^2 + 25\sigma_P^2,$$

we find for the 69 Newcomb stars $\sigma_m^2 = 6.943$, which is clearly greater than the maximum possible for $25\sigma_P^2$, *i.e.* 4.212 , and leaves σ_f^2 a minimum value of 2.631 . But if we take the Yale stars we find $\sigma_m^2 = 2.621$, which is *less* than the apparent value, 3.111 , of $25\sigma_P^2$, so that if the latter were correct we should have a negative value for σ_f^2 . This can only be satisfactorily accounted for on the assumption that f and P are not independent in our selection. In other words, although there is probably no organic relationship between intrinsic brightness and distance, still whenever we take a series of stars by any form of selection, we introduce a spurious correlation, which will generally of course be negative, between intrinsic brightness and parallax; that is to say, of the stars at a great distance—*i.e.* stars with small parallax—only those of great intrinsic brightness are admitted to our series.† The

* For both series together (245 stars) $V_{\pi} = 1.361$, or with maximum correction 0.962 , quite incompatible with 0.577 .

† This question of a spurious correlation arising from the manner in which the observer selects parallax stars is not without considerable interest, and worth following up in the case of the Yale stars. Our general relation is $m = f - 5P$, which leads us at once to: $\sigma_f^2 = \sigma_m^2 + 10\sigma_m\sigma_P r_{mP} + 25\sigma_P^2$ and $\sigma_f\sigma_P r_{fP} = \sigma_m\sigma_P r_{mP} + 25\sigma_P^2$. Now we can directly find σ_m , σ_P , and r_{mP} . Omitting Algol we have for the 121 Yale stars with positive parallax: $\sigma_m = 1.6190$, $\sigma_P = 0.3540$, $r_{mP} = -0.2179$, whence we deduce $\sigma_f = 2.1225$ and $r_{fP} = 0.6677$. Now (see p. 48), we have:

$$f = \text{a constant} - 2.5 \log_{10} P$$

modification which this idea requires in our theory will be developed in the following sections.

(8) In dealing with star series it is not unusual to include all stars up to a given magnitude, and counts have been made which are fairly reliable of all stars up to the 7.5 magnitude; indeed, we may be said to have practically complete lists of all the lucid stars (< 6 mag.). It will be clear, then, that if we can modify our theory, so that we do not include all stars up to a given distance from the sun, but all stars up to a given magnitude, we shall be able to compare it much more satisfactorily with observation. Now, this process of cutting off from consideration all stars above a given magnitude introduces a spurious correlation between magnitude and parallax, or between logarithm of parallax and the light emission.

We reduce the "density" of the more distant layers of stars, because the fainter stars in these layers do not reach the minimum admissible magnitude.

In order to reach any conclusion, it is, I think, needful to assume a law of distribution of the size and intrinsic brightness factor of the stars.

Returning to our equation for the magnitude, we have (see p. 48), neglecting any absorption factor

$$\begin{aligned} m &= 10 + 2.5 \log_{10} L_0 + 5 \log_{10} c - 2.5 \log_{10} F - 5 \log_{10} \pi \\ &= 10 + 2.5 \log_{10} L_0 - 2.5 \log_{10} F + 5 \mu \log_e D, \end{aligned}$$

where μ is again the modulus, and D is the distance. I shall put $\log_e D = x$, and instead of the f of the previous work write briefly y for

$$10 + 2.5 \log_{10} L_0 - 2.5 \log_{10} F.$$

Thus

$$m = y + 5\mu x,$$

and y will be a factor the variation of which depends solely on the size and intrinsic brightness of the individual star.*

Now, we need some law of frequency to distribute the character y , and it is not unreasonable to assume it in the first place to follow the same distribution—the Gaussian—which has been adopted by many astronomers for other stellar characters. I shall consider this point again; at present, it will be at least a guide to our theory, and indicate the possibility of

where F measures the amount of light emitted at the star. Hence if f and P are positively correlated, F and P will be negatively correlated, or we find in the Yale data that the light emitted and the parallax of the star are substantially correlated. This, of course, is an indirect result of the further stars being only included in the list when they have relatively greater absolute brilliancy than the near stars.

* x and y are used for the P and f of the earlier parts of this paper as more convenient for the following rather lengthy algebraic analysis.

extensions. We have now carefully to distinguish between the actual stars in the universe and those which will be found in our list, which we will suppose includes all, or at any rate a perfectly random sample of all, the stars up to magnitude m_0 .

Let \bar{y}_0 be the mean value of y for all the actual stars, and suppose the frequency of y given by

$$z = \text{const.} \times e^{-\frac{1}{2}(y-\bar{y}_0)^2/\sigma_y^2} = \text{const.} \times e^{-\frac{1}{2}\eta^2/\sigma_y^2},$$

if we write $\eta = y - \bar{y}_0$ for brevity.

Assuming a uniform distribution of stars of density ρ , we have between D and $D + \delta D$

$$4\pi\rho D^3\delta D \text{ stars} = 4\pi\rho D^3\delta \log_e D = 4\pi\rho e^{3x} dx.$$

Hence, since the hypothesis is that the intrinsic brightness of the stars and their distance from the sun are independent, it follows that the number of stars having characters lying between y and $y + \delta y$, x and $x + \delta x$ is of the form

$$\text{const.} \times e^{-\frac{1}{2}\eta^2/\sigma_y^2} e^{3x} dy dx = z_0 \times e^{-\frac{1}{2}\eta^2/\sigma_y^2 + 3x} dy dx, \text{ say.}$$

Now we are to take all possible values of x and y subject to the condition that $y + 5\mu x$ does not exceed m_0 . Clearly our limit is to be given by

$$m_0 - \bar{y}_0 = \eta + 5\mu x, \quad \text{or} \quad x = \frac{1}{5\mu} (\nu_0 - \eta),$$

where ν_0 is written for $m_0 - \bar{y}_0$ for brevity. Hence, if N be the total number of the selected stars,

$$\begin{aligned} N &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{\frac{1}{5\mu}(\nu_0 - \eta)} e^{-\frac{1}{2}\eta^2/\sigma_y^2 + 3x} dx dy \\ &= \frac{1}{5} z_0 \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\eta^2/\sigma_y^2 + \frac{3}{5\mu}(\nu_0 - \eta)} d\eta \\ &= \frac{1}{5} z_0 e^{\frac{3}{5\mu}(\nu_0 + \frac{3}{10} \frac{\sigma_y^2}{\mu})} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}(\eta + \frac{3}{5} \frac{\sigma_y^2}{\mu})/\sigma_y^2} d\eta \\ &= \frac{1}{5} z_0 e^{\frac{3}{5\mu}(\nu_0 + \frac{3}{10} \frac{\sigma_y^2}{\mu})} \sqrt{2\pi} \sigma_y. \end{aligned}$$

This determines $z_0 = \frac{3N}{\sqrt{2\pi}\sigma_y} e^{-\frac{3}{5\mu}(\nu_0 + \frac{3}{10} \frac{\sigma_y^2}{\mu})}$ and the constant of our frequency distribution. We can now proceed to find the mean $\bar{\eta}$ and the standard deviation σ_η of the emitted lights of the selected population of stars.

We have

$$\begin{aligned} N\bar{\eta} &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{\frac{1}{5\mu}(\nu_0-\eta)} \eta e^{-\frac{1}{2}\eta^2/\sigma_y^2 + 3x} dx d\eta \\ &= \frac{z_0}{3} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\left(\eta + \frac{3\sigma_y^2}{5\mu}\right)^2/\sigma_y^2} \left(\eta + \frac{3\sigma_y^2}{5\mu} - \frac{3\sigma_y^2}{5\mu}\right) e^{\frac{3}{5\mu}\left(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu}\right)} d\eta, \\ &= \frac{z_0}{3} e^{\frac{3}{5\mu}\left(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu}\right)} \left(-\frac{3\sigma_y^2}{5\mu}\right) \sqrt{2\pi} \sigma_y. \end{aligned}$$

Therefore, $\bar{\eta} = -\frac{3}{5\mu} \sigma_y^2$, and $\bar{y} = \bar{y}_0 + \eta = \bar{y}_0 - \frac{3\sigma_y^2}{5\mu}$.

Similarly

$$\begin{aligned} N(\sigma_\eta^2 + \bar{\eta}^2) &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{\frac{1}{5\mu}(\nu_0-\eta)} \eta^2 e^{-\frac{1}{2}\eta^2/\sigma_y^2 + 3x} dx d\eta \\ &= \frac{1}{3} z_0 \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\left(\eta + \frac{3\sigma_y^2}{5\mu}\right)^2/\sigma_y^2} \left(\eta + \frac{3\sigma_y^2}{5\mu} - \frac{3\sigma_y^2}{5\mu}\right)^2 e^{\frac{3}{5\mu}\left(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu}\right)} d\eta, \end{aligned}$$

or $\sigma_\eta^2 + \bar{\eta}^2 = \frac{1}{\sqrt{2\pi} \sigma_y} \left(\sqrt{2\pi} \sigma_y \sigma_y^2 + \frac{9\sigma_y^4}{25\mu^2} \sqrt{2\pi} \sigma_y \right),$

and accordingly $\sigma_\eta = \sigma_y$.

Thus, while the effect of cutting off the series at a given magnitude is to lower the mean light emitted, it makes no change whatever in the variability of light emitted. Neither the mean nor the standard deviation of the light emitted depends at all on the magnitude at which we close our series.

I now turn to the mean and variability of the logarithm of the distance.

$$\begin{aligned} N\bar{x} &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{\frac{1}{5\mu}(\nu_0-\eta)} e^{-\frac{1}{2}\eta^2/\sigma_y^2} x e^{3x} dx dy \\ &= \frac{1}{3} z_0 \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\eta^2/\sigma_y^2 + \frac{3}{5\mu}(\nu_0-\eta)} \left(\frac{1}{5\mu}(\nu_0-\eta) - \frac{1}{3} \right) d\eta \\ &= \frac{1}{3} z_0 \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\left(\eta + \frac{3}{5\mu}\sigma_y^2\right)^2/\sigma_y^2} \left[\frac{1}{5\mu}\nu_0 - \frac{1}{3} + \frac{3\sigma_y^2}{25\mu^2} - \frac{1}{5\mu}\left(\eta + \frac{3}{5\mu}\sigma_y^2\right) \right] d\eta \\ &\quad \times e^{\frac{3}{5\mu}\left(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu}\right)}. \end{aligned}$$

Hence

$$\bar{x} = \frac{1}{5\mu} \nu_0 - \frac{1}{3} + \frac{3\sigma_y^2}{25\mu^2} = \frac{1}{5\mu} \left(m_0 - \bar{y}_0 + \frac{3\sigma_y^2}{5\mu} \right) - \frac{1}{3} = \frac{1}{5\mu} (m_0 - \bar{y}) - \frac{1}{3},$$

$$\therefore \mu\bar{x} = \frac{1}{N} S(\log_{10} D) = \frac{1}{N} S(\log_{10} c - \log_{10} \pi) = \frac{1}{5} (m_0 - \bar{y}) - \frac{\mu}{3},$$

or $\bar{P} = \frac{\mu}{3} + \log_{10} c - \frac{1}{5} (m_0 - \bar{y}).$

This should be compared with the result on p. 50. It gives the modified form taken by the mean logarithm of the parallax.

Further, since $m = y + 5\mu x$,

$$\begin{aligned}\bar{m} &= \bar{y} + 5\mu\bar{x} \\ &= \bar{y}_0 - \frac{3\sigma_y^2}{5\mu} + m_0 - \bar{y}_0 + \frac{3\sigma_y^2}{5\mu} - \frac{5\mu}{3} \\ &= m_0 - \frac{5\mu}{3} = m_0 - 0.7238.\end{aligned}$$

Or, we have the remarkable general proposition that: *The mean of any random selection of stars not including any over the m_0 magnitude ought to be 0.7238 of a magnitude below this limiting value, if the stars are distributed uniformly through space.*

I next pass to the standard deviation of x . We have

$$\begin{aligned}N(\sigma_x^2 + \bar{x}^2) &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{1}{5\mu}(\nu_0 - \eta)} e^{-\frac{1}{2}\eta^2/\sigma_y^2} x^2 e^{3x} dx dy \\ &= \frac{1}{3} z_0 e^{\frac{3}{5\mu}(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu})} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}(\eta + \frac{3}{5\mu}\sigma_y^2)^2/\sigma_y^2} \left[\frac{1}{25\mu^2}(\nu_0 - \eta)^2 \right. \\ &\quad \left. - \frac{2}{3} \frac{1}{5\mu}(\nu_0 - \eta) + \frac{2}{9} \right] d\eta.\end{aligned}$$

Whence, after some reduction, we find

$$\sigma_x^2 = \frac{1}{9} + \frac{1}{25\mu^2} \sigma_y^2.$$

But it is easy to see that $\sigma_{\log D}$ is identical with $\sigma_{\log \pi}$, or σ_P/μ of our previous notation. Thus

$$25\sigma_P^2 = \frac{2}{9}\mu^2 + \sigma_y^2 = 0.5240 + \sigma_y^2.$$

We see accordingly that the quantity $25\sigma_P^2$ when we cut off at a given magnitude will for every magnitude be still constant, but it will exceed by the quantity σ_y^2 the "normal" value on the assumption that a random sample has been taken of all stars.

I now proceed to find the product moment of x and y with a view to determining their correlation.

$$\begin{aligned}N(\bar{xy} + \eta\bar{x}) &= z_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{1}{5\mu}(\nu_0 - \eta)} e^{-\frac{1}{2}\eta^2/\sigma_y^2 + 3x\eta} dx dy \\ &= \frac{1}{3} z_0 \int_{-\infty}^{+\infty} e^{-\frac{1}{2}(\eta + \frac{3}{5\mu}\sigma_y^2)^2/\sigma_y^2} \eta \left(\frac{1}{5\mu}(\nu_0 - \eta) - \frac{1}{3} \right) d\eta e^{\frac{3}{5\mu}(\nu_0 + \frac{3}{10}\frac{\sigma_y^2}{\mu})}.\end{aligned}$$

Whence, after some reductions, and substituting for \bar{x} and \bar{y} , we find:

$$\bar{xy} = -\frac{1}{5\mu} \sigma_y^2.$$

Reverting to our original equation,

$$m = y + 5\mu x,$$

we have

$$\bar{m} = \bar{y} + 5\mu \bar{x};$$

\therefore

$$m - \bar{m} = y - \bar{y} + 5\mu (x - \bar{x})$$

and

$$\begin{aligned}\sigma_m^2 &= \sigma_y^2 + 10\mu \bar{p}_{xy} + 25\mu^2 \sigma_x^2 \\ &= \sigma_y^2 - 2\sigma_y^2 + \frac{25\mu^2}{9} + \sigma_y^2 \\ &= \frac{25\mu^2}{9} = 0.5240.\end{aligned}$$

Thus the effect of cutting off our sample at a given magnitude produces a most important result; we replace the statement that σ_m^2 must always be greater than 0.5240 by a much more striking one: *The standard deviation of the magnitudes of a series of stars cut off at a given magnitude is constant, whatever that magnitude may be, and equal to the normal value of the $25\sigma_p^2$ parallax constant.*

We have here a very simple test of the uniform distribution of the stars through space.

I return to the result

$$\bar{p}_{xy} = -\frac{1}{5\mu} \sigma_y^2.$$

But

$$r_{xy} = \bar{p}_{xy} / \sigma_y \sigma_x = -\frac{1}{5\mu} \frac{\sigma_y}{\sigma_x} = -\frac{\sigma_y}{5\sigma_p} = -\frac{1}{\sqrt{1 + 0.524/\sigma_y^2}}.$$

There is thus always a *negative* correlation between x and y , which again means a positive correlation between the logarithm of the parallax and y , or, finally, a negative correlation between the logarithm of the parallax (or the parallax) and light actually emitted. In other words, cutting off at a given magnitude has introduced a spurious correlation between parallax and light emitted, between a star's distance from the sun and its size and intrinsic brightness. It is not probable that such a relationship actually exists in the totality of the stellar universe, but it should be apparently demonstrable in all actual collections of stars. For example, suppose the maximum light to be emitted by stars belonging to certain spectral (or colour) classes, then we should expect to find a correlation between parallax and spectral class of the above character. I think this "cutting off at a given magnitude" is most probably the source of the fairly high correlation (0.36) already noted by me as existing for the Yale observations between spectral class and parallax.*

* 'Monthly Notices, R.A.S.,' vol. 68, p. 428, 1908.

Further, this cutting off at a given magnitude will also modify the natural relationship between magnitude and parallax. Taking

$$m - \bar{m} = y - \bar{y} + 5\mu(x - \bar{x})$$

and multiplying by $(x - \bar{x})$, summing and dividing by the number of pairs in the usual way, we have

$$\begin{aligned}\bar{p}_{mx} &= \sigma_m \sigma_x r_{xm} = \bar{p}_{xy} + 5\mu \sigma_x^2 \\ &= -\frac{1}{5\mu} \sigma_y^2 + \frac{5\mu}{9} + \frac{1}{5\mu} \sigma_y^2 = \frac{5\mu}{9}.\end{aligned}$$

Thus, $\bar{p}_{mx} = 0.2413$, and is a constant.

Further, since $\sigma_m = \frac{5}{3}\mu$, we have

$$r_{xm} = \frac{1}{3} \frac{1}{\sigma_x} = \frac{1}{\sqrt{1 + \frac{9}{25\mu^2} \sigma_y^2}} = \frac{1}{\sqrt{1 + \frac{\sigma_y^2}{0.5240}}}.$$

Finally, the correlation of the logarithm of the parallax with the magnitude will be given by

$$r_{pm} = -\frac{1}{\sqrt{1 + \frac{\sigma_y^2}{0.5240}}}.$$

From the value previously given for $r_{xy} = -r_{py}$ we find:

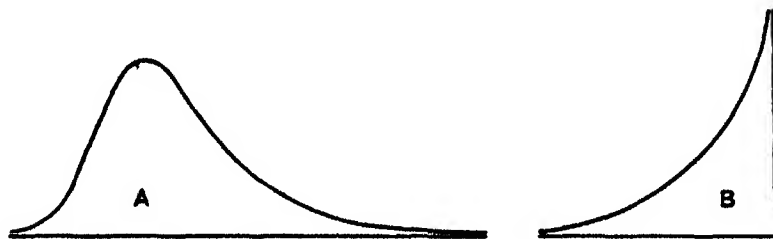
$$r_{py}^2 = 1 - r_{pm}^2,$$

or we are able from observable quantities to determine the correlation of parallax with the actual light emitted.* It may be noted that when there is a high correlation between parallax and magnitude, a low correlation will be found between parallax and actual light emitted.

(9) Before we proceed to compare the results of the preceding section with observation, it is fitting to consider how far they really involve the assumption made that the lights actually emitted by the stars obey a Gaussian frequency distribution. It is probably quite as legitimate to assume this as to suppose that stellar proper-motions follow the Gaussian law, but I wish to show that it is by no means needful to assume this in order to obtain the chief results reached in the previous section. I have taken the Gaussian curve in the first place because it has a certain sanction from astronomical usage, but our results are really much more general. It is open to anyone to argue that the universe is a dying system, that there are a majority of dark stars, or stars of small intrinsic brilliancy. If this be true, not only will the distri-

* In the case of the Yale stars $\sigma_y^2 = \sigma_f^2 = 4.5051$ and $\sigma_y^2/0.5240 = 8.5975$, and we find $r_{xm} = -0.3228$ and $r_{pf} = 0.9464$, against the observed values of -0.2179 and 0.6877 . This is, of course, further evidence that the Yale series is not a random sample "up to a given magnitude" of stars distributed uniformly through space.

bution of intrinsic brilliancies give a skew frequency curve, but the distribution of the logarithms of the factors which measure actually emitted lights will do the same thing. Accordingly we need, to cover this case, a frequency distribution far more general than the Gaussian, and one that can represent all degrees of skewness, from a type like A to one like B.



This is met by using the curve

$$z = z_0 \left(1 - \frac{\eta}{b}\right)^p e^{\eta},$$

which ranges from $\eta = b$ to $\eta = -\infty$, and which can take the form B if p be negative.

I have discussed this curve at length in a memoir in the 'Philosophical Transactions,' vol. 186, A, p. 373.

By supposing y or η to have this type of distribution, we shall at any rate determine how far our results are peculiar to the form or symmetry of a Gaussian frequency.

The form of the frequency surface will now be

$$z = z_0 \left(1 - \frac{\eta}{b}\right)^p e^{\eta + \frac{3}{5}\eta^2},$$

and we have at once

$$\begin{aligned} N &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0 - \eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\eta + \frac{3}{5}\eta^2} d\eta d\eta \\ &= \frac{1}{5} z_0 \int_{-\infty}^b \left(1 - \frac{\eta}{b}\right)^p e^{\left(\gamma - \frac{3}{5\mu}\right)\eta + \frac{3}{5\mu}\eta^2} d\eta. \end{aligned}$$

Assume $\zeta = \left(\gamma - \frac{3}{5\mu}\right)(b - \eta) = \lambda \left(1 - \frac{\eta}{b}\right)$, so that $\lambda = b \left(\gamma - \frac{3}{5\mu}\right)$, and we have

$$N = \frac{1}{5} z_0 e^{\frac{3}{5\mu}\lambda^2 + \lambda} \frac{b}{\lambda^{p+1}} \int_0^\infty \zeta^p e^{-\zeta} d\zeta = \frac{1}{5} z_0 \frac{e^{b\gamma + \frac{3}{5\mu}(\nu_0 - b)b}}{\lambda^{p+1}} \Gamma(p+1).$$

Thus

$$z_0 = \frac{3 N \lambda^{p+1}}{b \Gamma(p+1)} e^{-b\gamma - \frac{3}{5\mu}(\nu_0 - b)b}.$$

Next:

$$\begin{aligned} N\bar{\eta} &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0 - \eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\gamma\eta + 3x\eta} dx d\eta \\ &= \frac{1}{3} z_0 \frac{e^{b\gamma + \frac{3}{5\mu}(\nu_0 - b)} b}{\lambda^{p+1}} \int_0^\infty \xi^p e^{-\xi} b \left(1 - \frac{\xi}{\lambda}\right) d\xi, \\ \bar{\eta} &= \frac{b}{\Gamma(p+1)} \int_0^\infty \xi^p e^{-\xi} \left(1 - \frac{\xi}{\lambda}\right) d\xi \\ &= b \left(1 - \frac{p+1}{\lambda}\right). \end{aligned}$$

Now η is measured from the mean value, and therefore it is needful that* $p+1 = b\gamma$. Hence

$$\bar{\eta} = b \left(1 - \frac{b\gamma}{\lambda}\right) = -\frac{3}{5\mu} \frac{b^2}{\lambda} = -\frac{3}{5\mu} \frac{p+1}{\gamma^2} \frac{1}{1 - \frac{3}{5\mu\gamma}}.$$

Next

$$\begin{aligned} N(\sigma_\eta^2 + \bar{\eta}^2) &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0 - \eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\gamma\eta + 3x\eta} \eta^2 dx d\eta \\ &= \frac{1}{3} z_0 \frac{e^{b\gamma + \frac{3}{5\mu}(\nu_0 - b)} b}{\lambda^{p+1}} \int_0^\infty \xi^p b^2 \left(1 - \frac{2\xi}{\lambda} + \frac{\xi^2}{\lambda^2}\right) e^{-\xi} d\xi \end{aligned}$$

Hence
$$\sigma_\eta^2 + \bar{\eta}^2 = b^2 \left(1 - \frac{2}{\lambda} (p+1) + \frac{(p+2)(p+1)}{\lambda^2}\right)$$

and
$$\begin{aligned} \sigma_\eta^2 &= \frac{b^2(p+1)}{\lambda^2} = \frac{p+1}{\gamma^2} \left(1 - \frac{3}{5\mu\gamma}\right)^{-2} \\ &= \sigma_y^2 \left(1 - \frac{3}{5\mu\gamma}\right)^{-2}, \dagger \end{aligned}$$

that is
$$\sigma_\eta = \sigma_y \left(1 - \frac{3}{5\mu\gamma}\right).$$

Further, we may write

$$\bar{\eta} = -\frac{3}{5\mu} \sigma_y^2 \left(1 - \frac{3}{5\mu\gamma}\right).$$

Thus σ_η and $\bar{\eta}$ differ from the values on the Gaussian hypothesis, i.e. σ_y and $-\frac{3}{5\mu}\sigma_y^2$, by the introduction of the factor $1/\left(1 - \frac{3}{5\mu\gamma}\right)$, which becomes unity when $\gamma = \infty$. Still the two† general propositions remain true, i.e. that

* 'Phil. Trans.,' A, vol. 186, p. 374.

† $\sigma_y^2 = (p+1)/\gamma^2$; see *loc. cit.*, p. 373.

when we cut off our series at a given magnitude, the mean of the actual lights emitted is reduced by a constant quantity, and the variability of these lights is constant, whatever be that magnitude.

Turning next to the mean and variability of the logarithm of the distance, we find

$$\begin{aligned} N\bar{x} &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0-\eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\gamma\eta + \frac{1}{5\mu}x} dx d\eta \\ &= \frac{\frac{1}{5}z_0 e^{b\gamma + \frac{3}{5\mu}(\nu_0-b)} b}{\lambda^{p+1}} \int_0^\infty \zeta^p \left(\frac{\nu_0}{5\mu} - \frac{1}{3} - \frac{b}{5\mu} + \frac{b}{5\mu} \frac{\zeta}{\lambda} \right) e^{-\zeta} d\zeta, \end{aligned}$$

Hence

$$\begin{aligned} \bar{x} &= \frac{\nu_0}{5\mu} - \frac{1}{3} - \frac{b}{5\mu} + \frac{b}{5\mu\lambda} (p+1), \\ &= \frac{\nu_0}{5\mu} - \frac{1}{3} + \frac{3}{25\mu^2} \frac{b}{\gamma - \frac{3}{5\mu}}, \\ &= \frac{\nu_0}{5\mu} - \frac{1}{3} + \frac{3}{25\mu^2} \frac{\sigma_y^2}{1 - \frac{3}{5\mu\gamma}}, \end{aligned}$$

which differs from the Gaussian frequency result solely by the presence of the factor $1 - \frac{3}{5\mu\gamma}$ in the denominator of the last term.

Clearly we can write

$$\bar{x} = \frac{1}{5\mu} (m_0 - y_0) - \frac{1}{3} - \frac{1}{5\mu} \bar{\eta},$$

leading, as on p. 59, to the result

$$\bar{P} = \frac{1}{5}\mu + \log_{10} c - \frac{1}{5} (m_0 - \bar{\eta}).$$

Now $\bar{\eta}$ is a constant whatever be m_0 , for it equals $y_0 - \bar{\eta}$. Hence the mean logarithm of the parallax, when we increase the magnitude at which we terminate our series, decreases by $\frac{1}{5}$ (difference of cutting off magnitudes).

Proceeding next to the value of σ_x , we have

$$\begin{aligned} N(\sigma_x^2 + \bar{x}^2) &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0-\eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\gamma\eta + \frac{1}{5\mu}x} x^2 dx d\eta \\ &= \frac{1}{5}z_0 \frac{e^{b\gamma + \frac{3}{5\mu}(\nu_0-b)} b}{\lambda^{p+1}} \int_0^\infty \zeta^p \left(\frac{1}{25\mu^2} (\nu_0 - \eta)^2 - \frac{2}{3} \frac{1}{5\mu} (\nu_0 - \eta) + \frac{2}{9} \right) e^{-\zeta} d\zeta. \end{aligned}$$

Substituting for η in terms of ζ , integrating out and using the above value of \bar{x} , we find after some rather lengthy reductions that

$$\sigma_x^2 = \frac{1}{9} + \frac{1}{25\mu^2} \sigma_y^2 \left(1 - \frac{3}{5\mu\lambda}\right)^{-2} = \frac{1}{9} + \frac{1}{25\mu^2} \sigma_\eta^2.$$

We have then, as on p. 60,

$$25\sigma_P^2 = \frac{25}{9}\mu^2 + \sigma_\eta^2 = 0.5240 + \sigma_\eta^2 = 0.5240 + \sigma_y^2 \left(1 - \frac{3}{5\mu\gamma}\right)^{-2}.$$

Thus, as before, $25\sigma_P^2$ is a constant quite independent of m_0 , but exceeding its "normal" value by a fixed amount.

We may add here the value of the mean magnitude. As on p. 60

$$\begin{aligned}\bar{m} &= \bar{y} + 5\mu\bar{x} \\ &= y_0 - \frac{3}{5\mu}\sigma_y^2 \left(1 - \frac{3}{5\mu\gamma}\right)^{-1} + \nu_0 - \frac{5\mu}{3} + \frac{3}{5\mu}\sigma_y^2 \left(1 - \frac{3}{5\mu\lambda}\right)^{-1} \\ &= m_0 - \frac{5\mu}{3} = m_0 - 0.7238.\end{aligned}$$

Thus our general proposition of p. 60, that the mean magnitude of a system of stars up to a given magnitude is always less by 0.7238 than that magnitude, is established on the broader basis of non-Gaussian variability.

Lastly, I take the product moment of x and η

$$\begin{aligned}N(\bar{p}_{xy} + \bar{x}\bar{y}) &= z_0 \int_{-\infty}^b \int_{-\infty}^{\frac{1}{5\mu}(\nu_0 - \eta)} \left(1 - \frac{\eta}{b}\right)^p e^{\gamma\eta + 3x} \eta x dx d\eta \\ &= \frac{1}{3} z_0 \frac{e^{\gamma b + \frac{3}{5\mu}(\nu_0 - b)} b^3}{\lambda^{p+1}} \int_0^\infty \zeta^p \left(1 - \frac{\zeta}{\lambda}\right) \left\{ \frac{1}{5\mu} \left(\nu_0 - b + \frac{b\zeta}{\lambda}\right) - \frac{1}{3} \right\} e^{-\zeta} d\zeta,\end{aligned}$$

whence, integrating on the same lines as before, by aid of the Γ -function, we find

$$\bar{p}_{x\eta} = -\frac{b^2}{5\mu\lambda^2}(p+1) = -\frac{1}{5\mu}\sigma_\eta^2 = -\frac{1}{5\mu} \frac{\sigma_y^2}{\left(1 - \frac{3}{5\mu\gamma}\right)^2}.$$

But

$$\begin{aligned}\sigma_m^2 &= \sigma_\eta^2 + 10\mu\bar{p}_{x\eta} + 25\mu^2\sigma_x^2 \\ &= \sigma_\eta^2 - 2\sigma_\eta^2 + \frac{25\mu^2}{9} + \sigma_\eta^2 \\ &= \frac{25\mu^2}{9} = 0.5240.\end{aligned}$$

Thus, precisely as before with the Gaussian law, we have obtained with this more general frequency the same result, namely, whatever be the magnitude at which we cut off, the standard deviation of the magnitudes of the series is constant and equal to the "normal" value of $25\sigma_P^2$ for an unselected universe.

We may conclude with the correlations

$$r_{xy} = -\left(1 + \frac{0.5240}{\sigma_\eta^2}\right)^{-\frac{1}{2}} = -r_{Py},$$

$$r_{xm} = \left(1 + \frac{\sigma_\eta^2}{0.5240}\right)^{-\frac{1}{2}} = -r_{Pm},$$

and

$$r_{xy}^2 = 1 - r_{Pm}^2.$$

It follows therefore that all the results previously obtained for a Gaussian distribution hold for the much more general type of frequency now adopted. The only differences depend upon slight changes involving the constant factor

$$\left(1 - \frac{3}{5\mu\gamma}\right).$$

The distribution I have selected for the emitted lights enables us to suppose brilliant stars or even dark stars to be in a majority. It is sufficiently wide, I think, to cover any probable distribution of the intrinsic brilliancies of the stellar universe very closely. The main conclusions, however, that

$$\bar{m} = m_0 - 0.7238, \quad \sigma_m^2 = 0.5240,$$

I suspect to be capable of simple proofs independent of any assumption as to frequency distribution. I have not stayed to seek for such proofs, but given those by which I have myself reached these results. They provide the mean magnitude and magnitude variability of any catalogue or random sample of stars up to a given magnitude, for example, of all the stars which could be seen with a telescope of given aperture—of course, on the assumption that the stars are distributed at random through space. They are thus fundamental in determining whether such a distribution is the actual one or not. There are two points to be borne in mind here. First our discussion is perfectly independent of direction, we have only supposed that spherical shells about the sun as centre, if of equal volume, contain the same number of stars. These stars may or may not be clustered in individual shells towards one or more directions. Our propositions apply to the frequency at each distance, and have no relation to direction.

Secondly, we have seen that

$$\sigma_m^2 = 0.5240 = 25\sigma_p^2,$$

or takes the value that $25\sigma_p^2$ does for a uniform spherical stellar universe. I strongly suspect that this principle is general, namely, that the value of σ_m^2 when we cut off at a given magnitude is equal to the value of the parallax constant, $25\sigma_p^2$, for the total universe, whatever be its assumed form. If this be true, then the values given in the table on p. 54 will have additional meaning. They show the modifications possible in σ_m^2 when we suppose the stellar universe spheroidal rather than spherical in form—still maintaining a uniform distribution of stars. As I have indicated, an ellipsoidal rather than a spherical form for the stellar universe appears to raise the value of $25\sigma_p^2$ and accords more closely, as we shall see, with experience. I hope later to discuss how far $\sigma_m^2 = 25\sigma_p^2$ is either approximately or absolutely true for other than spherical stellar distributions.

(10) It remains now to consider how far the results reached in the

previous sections, (8) and (9), are consistent with observation. Luckily we possess very accurate counts of the stars up to magnitude 7.25. The best of these is probably that due to Prof. Pickering,* and I shall make use of that here. Even if in some of the categories the counts are not absolutely accurate, the divergencies will occur in the higher magnitudes, where they will, owing to the large numbers dealt with, make no impression on the values of the means or standard deviations.

The table below gives the frequency up to each magnitude in the second column. In the third and fourth columns are given the actual and theoretical mean magnitudes up to the magnitude in the first column, the fifth and sixth columns give the square of the actual and theoretical standard deviations. The seventh and eighth columns give the differences of the observed and calculated values registered in the third to sixth columns. The means and standard deviations were calculated by the summation method discussed by Palin Elderton.†

1.	2.	3.	4.	5.	6.	7.	8.
Up to magnitude.	Observed frequency.	Mean.		Sq. standard deviation.		Differences.	
		Observed.	Theoretical.	Observed.	Theoretical.	$\Delta m.$	$\Delta \sigma_m^2.$
0.25	5	—	—	—	—	—	—
0.75	10	—	—	—	—	—	—
1.25	18	—	—	—	—	—	—
1.75	32	—	—	—	—	—	—
2.25	58	1.440	1.526	0.423	0.524	-0.086	-0.101
2.75	106	1.914	2.026	0.512	0.524	-0.112	-0.012
3.25	193	2.409	2.526	0.571	0.524	-0.117	+0.047
3.75	336	2.874	3.026	0.619	0.524	-0.152	+0.005
4.25	589	3.357	3.526	0.664	0.524	-0.169	+0.140
4.75	1067	3.860	4.026	0.689	0.524	-0.157	+0.166
5.25	1972	4.388	4.526	0.691	0.524	-0.138	+0.167
5.75	3562	4.885	5.026	0.688	0.524	-0.141	+0.164
6.25	6284	5.368	5.526	0.695	0.524	-0.158	+0.171
6.75	11004	5.853	6.026	0.711	0.524	-0.173	+0.187
7.25	17955	6.297	6.526	0.748	0.524	-0.220	+0.224

It will be obvious from this table that while our formulæ $\sigma_m^2 = 0.524$ and $\bar{m} = m_0 - 0.724$, express approximately the truth (never differing by a quarter of a magnitude from it), yet the observed values differ sensibly and almost regularly from the calculated values—the higher the limiting magnitude the greater is the divergence. That is to say, the more stars we take into our consideration,

* "Distribution of the Stars," 'Annals of Harvard College Observatory,' vol. 48, pp. 149—185.

† 'Biometrika,' vol. 4, pp. 374—8.

the less accurate appears the assumption of the uniform distribution of the stars through space. I think we are fully justified on the basis of this table in stating that a random distribution of the stars through a spherical space is inconsistent with observed facts. Or, if such a random distribution exists, then there must be a correlation between distance and intrinsic brilliancy. Such an apparent correlation would be produced, of course, if light were to any extent absorbed in its transmission through space. The few stars of lower than the third magnitude may be reasonably supposed uniformly scattered through space, since they fairly closely satisfy the necessary conditions; beyond this magnitude we have *continuous* deviations which cannot possibly be looked upon as the random or irregular variations from a chance scattering.

(11) It may hardly be needful to bring further evidence that the stellar universe is not a random distribution through space of stars of varying size and intrinsic brilliancy. But it may still be of interest to illustrate one or two points from different material. I chose Burnham's 'Catalogue of Double Stars' because the selection there is of a somewhat different character to a star count, and further because there are records of stars up to a much higher magnitude. Confining our attention to primaries only, we have the following table:—*

Range of magnitude.	Number of stars.	\bar{m}^*	σ_m^2
Up to 6.2	813	5.204 (5.496)	1.008
" 8.2	4947	7.112 (7.496)	1.087
" 10.2	9711	7.979 (9.496)	1.385
" 12.2	9807	8.025 (11.496)	1.517
" 15.5	9900	8.042 (14.796)	1.596

* Theoretical means are placed in brackets; of course, no stress must be laid on more than the first two or three entries, and the whole evidence is not comparable with that from total counts.

It is clear that σ_m^2 here starts a good deal higher than the star counts leave off. But the general tendency is the same, the mean does not increase fast enough, and the variability, instead of remaining constant, tends to rapidly increase. Very faint doubles may easily be overlooked, but, I think, this is far from explaining the *whole* evidence of the above table, which is in the same direction as we have seen in the total counts of lower magnitudes. Double stars even more markedly than the whole stellar system do not seem to obey the condition of uniform distribution through space.

Thus from several directions we find evidence accumulating that the stars cannot, without regard to their size or intrinsic brilliancy, be considered as on

* I owe this table to the kindness of Mr. P. F. Everitt.

the average uniformly distributed through space. The only way I can see to save such an hypothesis is either to assume a limited universe, not spherical in form, or to suppose light absorbed in transit. It will be interesting to inquire further into the effect of modifying the form of a uniformly dense stellar universe, and secondly to inquire whether when we confine our stars to one spectral class we get any difference in the general nature of the above deviations.

In conclusion, I must acknowledge my very great indebtedness to Miss Julia Bell, M.A., for much aid in the laborious calculations, of which only the final results are tabled in this paper; to Mr. E. Cunningham for a suggestion as to the best form in which to put the integral required in the case of the oblate spheroid universe; and to Mr. C. H. Williams for mechanically integrating and tabling both oblate and prolate spheroid integrals.

The Liberation of Helium from Minerals by the Action of Heat.

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(Communicated by Prof. the Hon. R. J. Strutt, F.R.S. Received April 12,—Read April 28, 1910.)

Introductory.

It is well known that the helium contained in radio-active minerals can be liberated by the action of heat, but, hitherto, no exact quantitative experiments have been made on the subject, and it was thought desirable to conduct such experiments with a view:—

- (1) To ascertain whether heat may not be used as a substitute for chemical methods in the case of minerals and rocks for which those methods are not convenient,* and, if so, the temperatures necessary.
- (2) To throw, if possible, more light on the way in which the gas is retained within the mineral.

A number of experiments have been made by Travers† on cleveite and

* Chemical methods break down (a) when the helium-content is very small, so that large quantities have to be treated to liberate a measurable volume of gas; (b) when no simple reaction is available, or when such a reaction gives rise to large volumes of other gases. Iron sulphide, which occurs in many geological horizons, is an example of this.

† Travers, 'Roy. Soc. Proc.' A, vol. 64, p. 140. The minerals were heated to redness in a hard glass tube, and, therefore, to a temperature not exceeding 600° C.

other minerals, which showed that about half the whole helium-content was given up at a red heat, and this estimate was used by Prof. Strutt* in his earlier work on the helium-content of various minerals. For those experiments it was not worth while to go more deeply into the matter, the more so as chemical methods suitable for many substances were at hand.

The state in which helium exists in rocks in which it has accumulated must in every case be essentially the same, and therefore it will be permissible to apply the general conclusions deduced from experiments on materials whose helium-content may be obtained chemically, to minerals for which those methods are inconvenient or impossible. However, experiments have been made on two very dissimilar substances, namely, monazite, which contains a comparatively small proportion of helium, and thorionite, a mineral crystallising in cubes, and containing a relatively large amount thereof. In spite of this difference, the results obtained from the two substances are in complete agreement.

The method of the experiments was to heat the mineral *in vacuo* to a known temperature, and to measure the volume of gas liberated at known times from the commencement of the experiment. Each temperature was maintained till the gas released during the course of one day was too small for measurement.

Apparatus.

This consists of two parts, that concerned with the heating of the mineral, and that concerned with the gas evolved. The essentials of both are shown, but not to scale, in fig. 1.

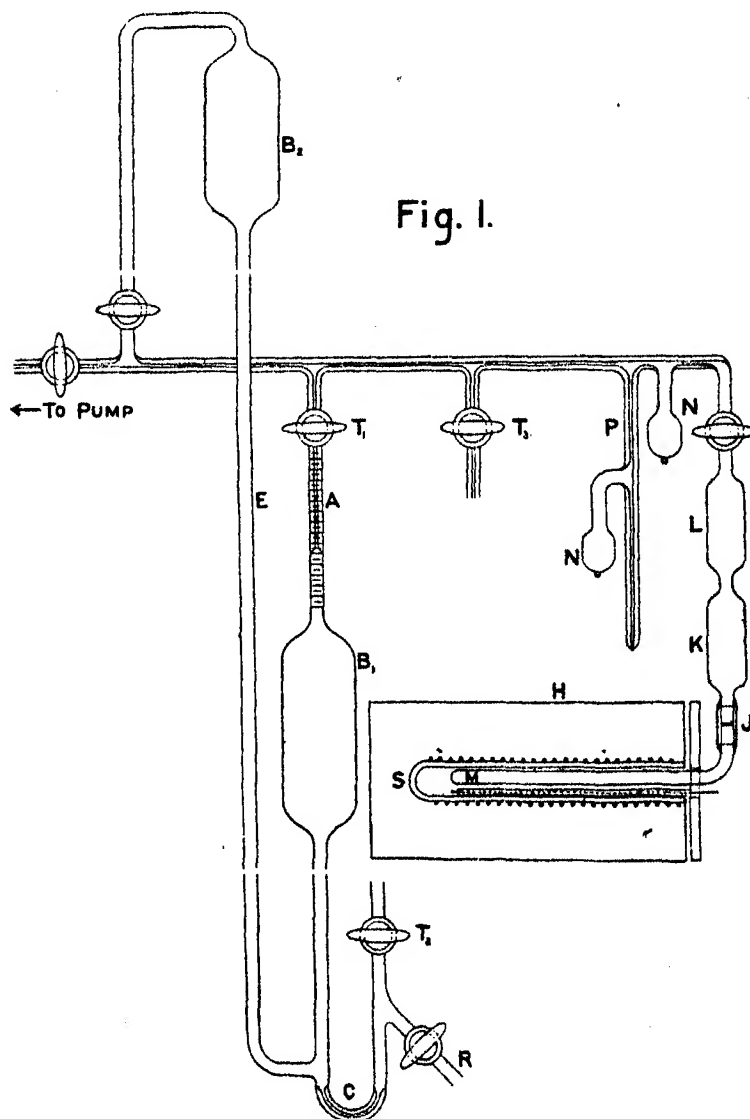
A. The heater H consisted of a single layer of nickel wire wound over a fused silica tube S about 18 inches long, and covered with several layers of asbestos cloth. The winding was arranged, as far as possible, to give a uniform temperature along the whole length of the tube. Fairly thick wire (gauge 21) was necessary to stand the prolonged heating required—the temperature rising to 1000° and 1200° C., and lasting several weeks without cessation.

In Experiments I and II the temperatures were measured with a high range mercury thermometer; in III and IV, with a platinum resistance thermometer and a Whipple indicator kindly lent by Prof. Callendar. Prolonged heating at 1000° C., however, was found to have a deleterious effect on the glaze of the porcelain tube, and a platinum-platinum-rhodium thermocouple was made up and used in conjunction with a Cambridge thermocouple indicator. The couple was calibrated by comparison with the platinum thermometer.

In the earlier experiments the mineral was heated in ordinary glass tubing,

* Strutt, 'Roy. Soc. Proc.,' A, vol. 80, p. 572.

but it was soon found that only a small proportion of the helium was liberated at temperatures below the softening point of the glass, and, therefore, Jena glass tubes were used, the part M passing into the furnace, but not



filled with the mineral, being packed with sand to prevent the collapse of the walls, and plugged with glass wool to stop any sand particles being carried over by the gas. Temperatures up to 750° C. were thus practicable, but were not sufficient to release all the gas contained in the mineral. For higher

temperatures quartz tubes were used, in spite of the possible leakage of helium* through them. Air-tight connection between the quartz and glass tubing was made by rubber pressure tubing tightly wired and completely covered with Chatterton cement (J).

The furnace was closed by a piece of asbestos card, which served also to shield the cement joint and the cold junction of the thermocouple from heat radiation. In the ordinary course the temperature variation was not greater than 20°. On two occasions, when the cells supplying the current failed, the equivalent time of heating was calculated by interpolation from the quantity of gas evolved.

B. The gas was purified on its way to the measuring gauge by passing over caustic potash and phosphorus pentoxide contained in the tubes K and L respectively. This removed all the moisture and the greater part of the carbon dioxide; a final purification being effected by means of the sodium potassium electrodes N, N. The purity of the helium was determined by spectroscopic examination of the glow in the capillary tube P.

The volume of gas liberated was measured in a modified form of the McLeod gauge, described by Prof. Strutt in his paper previously mentioned. It consists essentially of a tube A graduated into equal lengths and calibrated, connected with a bulb B₁ whose volume is large compared with the rest of the apparatus. A glass reservoir filled with mercury is connected by rubber pressure tubing to the end of the tube R, and when this is lowered the mercury runs out of B₁, drawing in gas from the rest of the apparatus through the tap T₁. A few seconds being allowed for complete diffusion T₁ is closed, and the reservoir raised, thus compressing the gas into A where its volume is measured. The bulb B₂ being vacuous the difference in level of the mercury in A and E gives the pressure and therefore, the volume at standard pressure may be calculated. The volume so found requires to be multiplied by the ratio of the total volume of the apparatus to which gas has access to the total volume of the bulb B₁ in order to correct for the volume of gas not drawn into it. This ratio is found from the volume of gas pumped out from the respective parts by the Toepler pump used. When more gas has collected than is convenient for measurement in A, its volume is found, it is pumped out, and a fresh start is made, the new volumes being added to that removed. Any air bubbles that enter through R collect under the tap T₂, and are from time to time allowed to escape through it.

* Jacquierod and Perrot, 'Comptes Rendus,' 1904, vol. 2, p. 20. The rate of leak must be proportional to difference of pressure of helium on either side, which in experiments such as these is very small. The existence of a leak is shown, however, in the thorionite curve of fig. 3, at 1000° C.

The tap T_2 is connected to another set of purifying tubes through which gas can be admitted from the outside for measurement in the gauge.

Experiments and Results.

Monazite.—The mineral was ground in an iron mortar and sifted to a fairly uniform size—that of a coarse angular sand. The total helium-content being estimated at 1/10 c.c. per gramme, about 5 grammes were used as giving a convenient volume of gas for measurement in the gauge. Experiments I and II, which were of a preliminary character, showed that while at temperatures up to 500° C. there was a practical limit to the volume of gas given off, that volume was only a small fraction of the total content. In Experiment III the temperature was increased by a succession of stages, and it was intended to maintain each until the practical limit to the volume of gas liberated was attained; but for temperatures about 600° C. the time became so prolonged that it was necessary to increase the temperature without reaching the limit. In this experiment the mineral was heated to 720° C. only, but in Experiment IV, with a quartz tube, the temperature was taken at once to 900°, and then to 1200° C. Unfortunately, at the higher temperature the apparatus began to leak, and the volume liberated had to be calculated from a chemical determination of the volume of the residual gas.

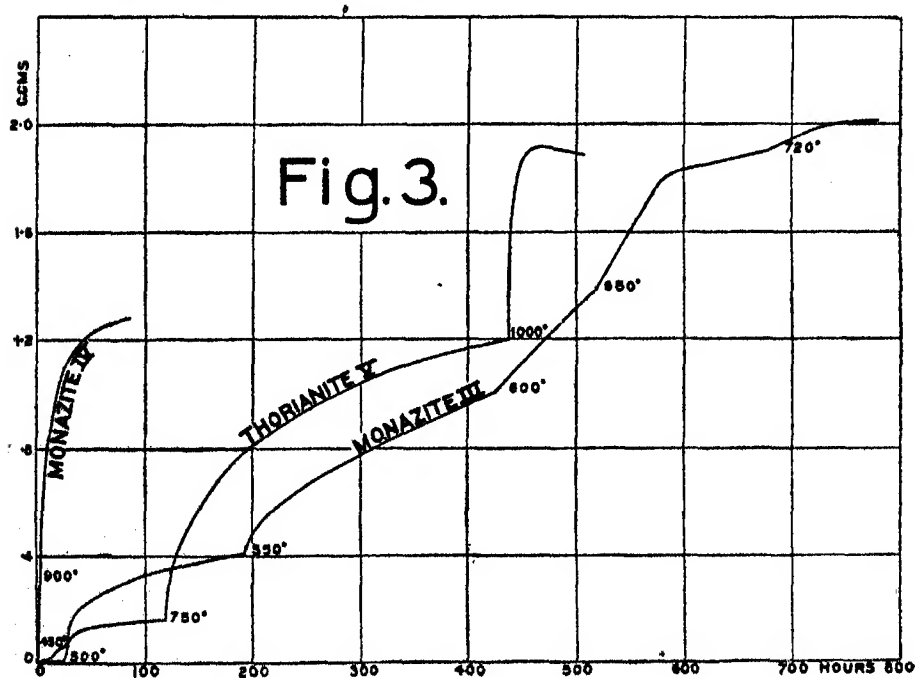
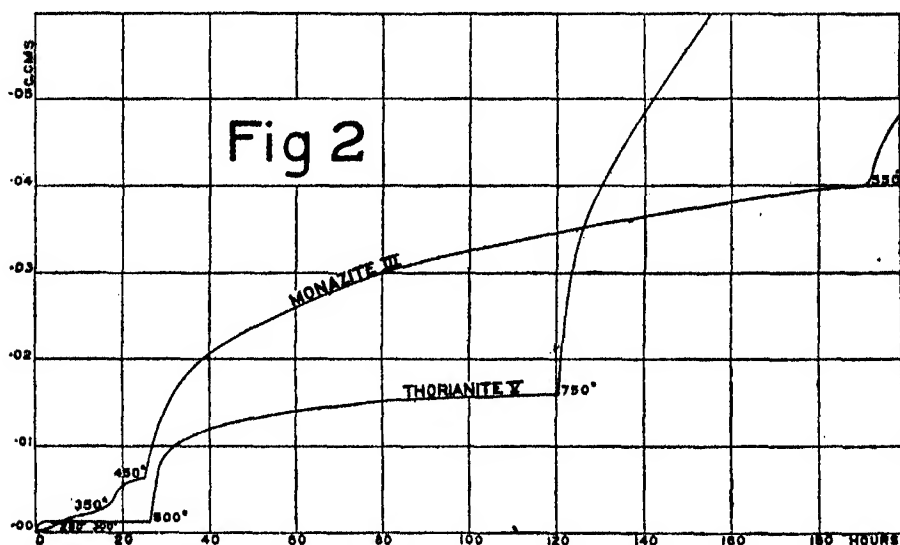
The initial volume was found by heating the ground mineral with sulphuric acid, in a closed tube exhausted of air,* to 120° C. for three weeks. The gas so liberated was introduced into apparatus through T_2 and treated in the usual way. The only visible change in the mineral was that the colour, originally brown, became slaty blue.

Thorianite.—The helium-content being approximately 9 c.c. per gramme, one-fifth of a gramme of the mineral was used, perfect crystals only being taken. But one experiment was necessary, as it was possible to reach the practical limit at each temperature. At the conclusion, six of the crystals used were splintered into laminæ and two remained unchanged.

The results are shown in the curves (figs. 2, 3), and in the table which gives the percentage of the whole content extracted at each temperature. It will be seen that in every case after a rise in temperature there is an initial rush of gas followed by a slower emission; but there seem to be three distinct stages. At the lower temperatures the first rush brings nearly all the gas that will ever come at the temperature, and the practical limit is quickly reached. At temperatures somewhat higher the first rush is followed by a prolonged and fairly rapid liberation of gas. In this stage the greater part of the gas is evolved. Finally, at the highest temperatures employed, the

* Travers, 'Study of Gases,' p. 34.

remainder of the gas is evolved almost at once. If heat is to be used as a practical method of liberating helium from minerals, it is necessary that a temperature corresponding to this third stage should be reached. The curves, however, are of little use for indicating the way in which the gas is retained



Experiment No.	Mineral.	Temp.	Time for which temperature was maintained. State at that time.	Volume of helium* evolved.	Maximum volume* per gramme obtainable.	Percentage of total content.
III	Monazite (5.35 grammes)	° C.				
		280	Maximum reached in 12 hrs.	0.021	0.0039	0.7
		350	Maximum reached in 12 hrs.	0.065	0.012	2.1
		450	After 170 hrs. gas still evolved very slowly.	0.400	0.071	12.7
		550	After 250 hrs. no sign of limit.	1.00	—	—
		650	After 160 hrs. still evolving at 1 cub. mm. per hour.	1.91	—	—
IV	Monazite (2.62 grammes)	720	After 100 hrs. still evolving, but limit probable in 50 hrs.	2.05	0.354	68.6
		900	In 90 hrs. practical limit reached.	1.30	0.496	88.5
V	Thorianite (0.199 grammes 8 cubes)	1200	After 4 hrs. only 0.008 cc./gr. left in mineral.	—	0.55†	98.3
		300	Practical limit in 5 hrs.	0.0135	0.068	0.7
		500	Practical limit in 80 hrs. ...	0.165	0.819	8.5
		750	Practical limit in 320 hrs. ...	1.3	6.00	62.3
		1000	All gas liberated in 30 hrs....	1.92	9.65	100.0

* These volumes are measured at 17° C. and 30 inches of mercury.

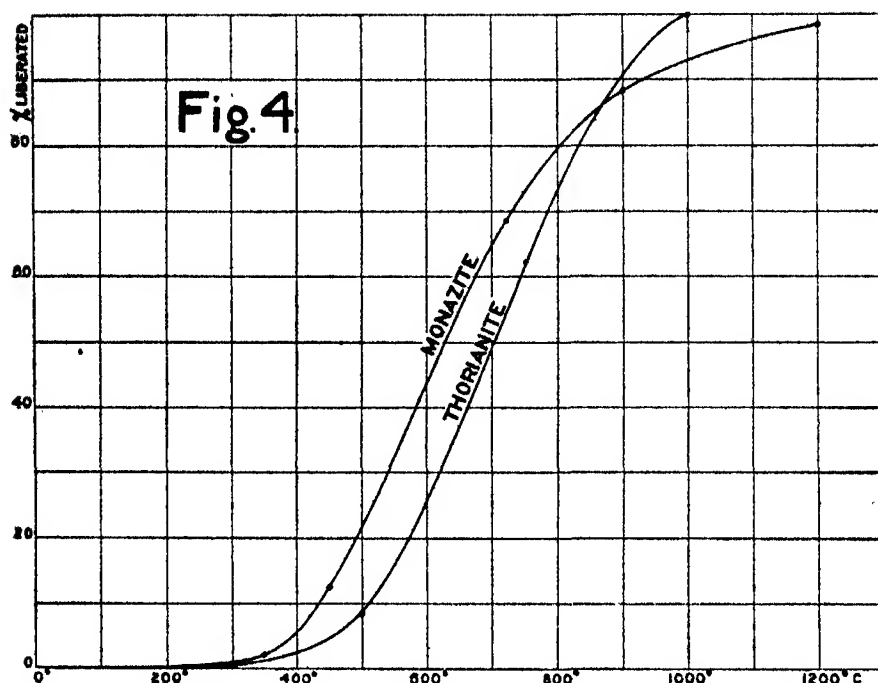
† Total content 0.56 c.c. per gramme.

within the mineral, as on any hypothesis it is to be expected that, when a fresh temperature is taken up, the rate at which equilibrium is attained will be greater initially than when the final conditions are more nearly reached.

The curves in fig. 4 show the percentage of the whole helium-content liberated at each temperature, neglecting the very slow "leakage" that takes place when the temperature has been maintained for some time. That these curves should be somewhat complex is to be expected when it is considered that the escape of the gas must be governed by several independent circumstances. When a helium atom is expelled from the atom of the radio-active substance it is brought to rest by collisions with neighbouring atoms, and the result, after the process has been in operation for a long time, would be a homogeneous mixture—in fact, a solution of the gas in the solid; but if the mineral contains cavities or pores, there will be an accumulation of helium atoms therein. The point to be settled is, has any such concentration occurred? If so, to what extent? Experiments by Gray* on the liberation of helium from thorianite by grinding make it probable that at least 30 per cent. of the gas in that mineral is contained in exceedingly minute cavities.

Consider the effect of an increase of temperature; it will result: (α) in an

* Gray, 'Roy. Soc. Proc.,' A, vol. 82, 1909, p. 306.



increased rate of diffusion of gas through the mineral, and probably a rapid escape from the surface layers; (b) in an increase of the pressure of the gas in the cavities, which will tend to the formation of cracks in the mineral just where they can best aid the escape of the gas; and finally, (c), owing to unequal expansions, minute cracks will develop in the crystal which may result in its ultimate disintegration.

A note may be here inserted on the pressures that must exist within a thorianite crystal. The density of thorianite is approximately 8.5 grammes per cubic centimetre, and as the helium-content is 9 c.c. per gramme, the volume concentration of the gas is considerable; but if—for the sake of illustration—it be supposed that only 30 per cent. of the whole is retained in cavities, and that those cavities occupy as much as one-tenth of the whole volume, then the pressures therein may be as great as 225 atmospheres, and this at 0° C. When the temperature is raised, this pressure must have a considerable effect in the development of cracks within the mineral.*

Now, consider the curves of fig. 4. Up to temperatures between 300° and

* To illustrate this it may be mentioned that when a thorianite crystal is heated to bright redness in a blow-pipe flame a shower of small fragments is thrown off, and the crystal may ultimately explode.

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400° C. the total quantity of gas practically obtainable is very small, and increases but gradually. It seems fair to assume that this may be due to simple diffusion of helium through the surface layers of the mineral. Above these temperatures the slope of the curves entirely change, and the quantity of gas obtainable becomes much greater. This is in agreement with the development of cracks within the mineral under the united influence of unequal expansion and of pressure, which is now more than twice its initial value. Finally, at much higher temperatures the slope again decreases, as would be expected in any case, owing to the great diminution in the quantity of gas present.

Thus it has been shown (1) that heat may be used to determine the total volume of helium contained in radio-active minerals if a sufficiently high temperature be reached ; and (2) that the laws governing the liberation of gas with temperature are at least in agreement with the supposition that a small proportion of the gas exists diffused through the mineral, and that the remainder is concentrated in very minute cavities within it.

In conclusion, I have to express my gratitude to Prof. Strutt for his encouragement and help throughout the course of these experiments.

On Scandium.—Part II.

By SIR WILLIAM CROOKES, D.Sc., LL.D., For. Sec. R.S.

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(Abstract.)

This is a continuation of the paper read in April, 1908,* in which, after describing the mode of extracting Scandia from the mineral wiikite, the principal salts, 23 in number, were described, their formulæ and analytical results being given in detail.

Since that publication, G. Eberhard,† of the Astrophysical Observatory, Potsdam, reasoning from the fact that the strongest lines of the Scandium spectrum are observed in the spectra of stars in diverse stages of development, has come to the conclusion that Scandium must be universally distributed on the earth. Investigating the arc spectra of 366 minerals and rocks, he obtained the remarkable result that Scandium in small quantities is actually one of the most widely distributed earth elements.

These results of Eberhard were quickly verified by Prof. R. J. Meyer,‡ Berlin University, who, in a preliminary paper, has described experiments on extracting Scandia from the Zinnwald wolframite. Prof. Meyer concludes that this wolframite contains from 0·14 to 0·16 per cent. of rare earths, and that these earths contain 0·30 to 0·33 per cent. of Scandia. Thus the original wolframite would contain about $0\cdot15/100 \times 0\cdot315/100 = 0\cdot04725/10,000$ or about 0·0005 per cent. of Scandia.

On reading Prof. Meyer's paper I examined the felspar and mica which were associated with the parcels of wiikite procured by me from Finland. The felspar contains a small percentage of rare earths, but no trace of Scandia could I detect on examining their photographed spectra, the dominant line, wave-length 3613·984, being entirely absent. The mica was found to contain about 1 per cent. of rare earths, and in the photographed spectrum the dominant lines of Scandium are plainly visible. From a comparison of the spectra with those taken of the rare earths from wiikite I should estimate the Scandia at about half that in the earths of the best black wiikite.

* 'Phil. Trans.,' vol. 209, pp. 15—46, March 4, 1908.

† 'Sitzungsber. Kgl. Preuss. Akad. Wissensch.,' 1908, vol. 38, p. 851.

‡ 'Zeit. für Anorg. Chem.,' vol. 60, p. 134, November 17, 1908; and 'Chemical News,' vol. 99, pp. 85, 97, February, 1909.

A specimen of wolframite from Zinnwald was found to contain less than 1 per cent. of rare earths, and in the photographed spectrum of these earths the dominant lines of Scandium were strong, accompanied by only the faintest trace of yttrium or ytterbium lines.

In the quantitative determination of the Scandia in the salts described in the present paper the residual earth was collected from the mother-liquor and a photograph taken of its spectrum. A comparison of the pair of spectra shows at once if any separation has been effected between the earths present. When separation is apparent further experimentation on a larger scale is reserved to a future occasion.

Scandium Iodate, $\text{Sc}(\text{IO}_3)_3 + 18\text{H}_2\text{O}$, is prepared by the metathesis of a soluble Scandium salt with ammonium iodate. It forms a white crystalline powder almost insoluble in water.

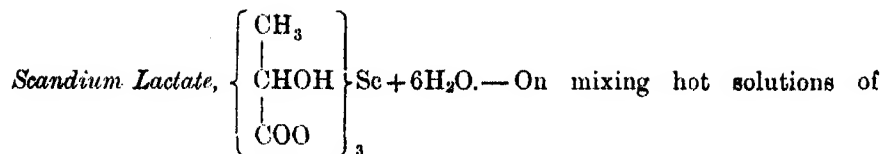
Scandium Sulphite, $\text{Sc}_2(\text{SO}_3)_3$, is a white insoluble powder formed by mixing a soluble Scandium salt with sodium sulphite. It is anhydrous and gradually decomposes on exposure to dry air.

Scandium Borate, ScBO_3 , is a white powder, having the appearance under the microscope of minute transparent spheres. In transmitted polarised light each spherulite shines like a point of light on the dark field when the analyser is crossed, each point alternately disappearing and reappearing as the stage is rotated.

Scandium Aurochloride, $3\text{ScCl}_3 \cdot 2\text{AuCl}_3 \cdot 21\text{H}_2\text{O}$, is prepared by mixing strong solutions of the component chlorides, and allowing the mixture to evaporate slowly over sulphuric acid in a vacuum desiccator. The double salt separates out in a felt-like mass of needle-shaped crystals of a yellow colour and very deliquescent.

Scandium Platinocyanide, $\text{Sc}_2[\text{Pt}(\text{CN})_4]_3 \cdot 21\text{H}_2\text{O}$, is formed by the metathesis in the cold of Scandium sulphate and barium platinocyanide. It crystallises out in large monoclinic prisms on a rhombic base, the angles of which are $81^\circ 20'$ and $98^\circ 40'$. They are very soluble in water, and are insoluble or nearly so in absolute alcohol, and frequently group themselves in rosettes. They are dichroic, crimson by transmitted light, and a rich metallic green by reflected light. The reflected and transmitted rays are oppositely polarised.

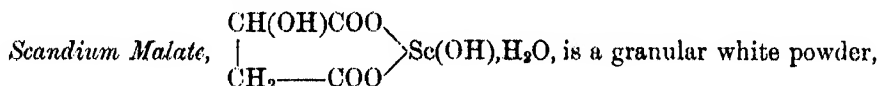
Scandium Mono-chloroacetate, $(\text{CH}_2\text{ClCOO})_2\text{ScOH} + 2\text{H}_2\text{O}$.—Scandium hydroxide, ground and well shaken with a cold aqueous solution of mono-chloroacetic acid, dissolves slowly and almost completely. The clear filtered solution, evaporated in the cold over sulphuric acid, deposits a crystalline crust, appearing under the microscope as flower-like groups of stellate crystals, and showing good colour when examined by polarised light.



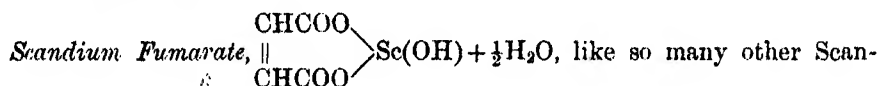
Scandium nitrate and ammonium lactate, the Scandium salt on cooling separates in white feathery crystals, slightly soluble in cold, more soluble in hot water, and easily soluble in ammonia.

Scandium Malonate, $\text{CH}_2 \begin{array}{c} \text{COO} \\ \diagup \quad \diagdown \\ \text{COO} \end{array} \text{Sc(OH)}$.—Scandium hydroxide dissolves readily in a cold aqueous solution of malonic acid, and the solution when heated deposits a semi-transparent granular precipitate, having no crystalline appearance under the microscope. This precipitate partially dissolves on cooling.

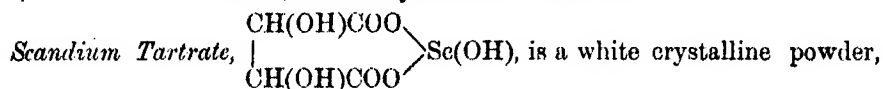
If this solution is boiled for some time a dense precipitate is formed, which on cooling does not re-dissolve.



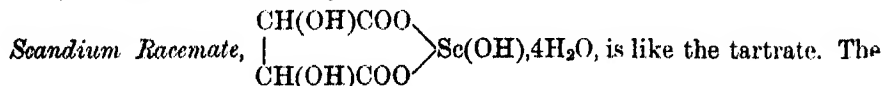
soluble in hot and difficultly soluble in cold water. It is easily soluble in ammonia, and is not precipitated from the ammoniacal solution by dilute acetic or malic acid.



dium salts, is more soluble in cold than in hot water. It is a white powder, appearing under the microscope as very minute spheres, slightly soluble in hot, more so in cold water, and easily soluble in ammonia.



insoluble in hot, slightly soluble in cold water, and insoluble in alcohol. Dried in a desiccator it is anhydrous.



two salts, however, are not quite similar. The racemate comes down less plentifully on boiling, and it is not anhydrous as is the tartrate, but contains four molecules of water, one of which is driven off at 115° .

Equal weights of tartaric and racemic acids were dissolved in separate bottles of water, and equal quantities of Scandium hydroxide added to each bottle, the amount being chosen so that all dissolved except a small quantity.

The two bottles were shaken in the cold for half an hour and filtered. The clear solutions were well boiled. A precipitate was formed in each, but that in the tartrate was double that in the racemate.

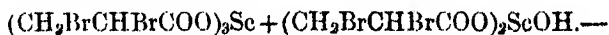
Scandium Lævo-tartrate, $\begin{array}{c} \text{CH(OH)COO} \\ | \\ \text{CH(OH)COO} \end{array} \text{Sc(OH),2H}_2\text{O}$, is prepared in a

similar way to the tartrate. Dried in a desiccator over sulphuric acid it contains one molecule of water. Dried in the air it contains two molecules of water.

Scandium Meso-tartrate, $\begin{array}{c} \text{CH(OH)COO} \\ | \\ \text{CH(OH)COO} \end{array} \text{Sc(OH),H}_2\text{O}$, is prepared by

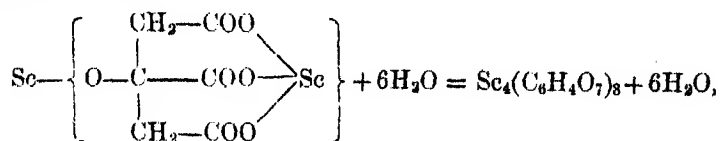
gently warming a slight excess of Scandium hydroxide with aqueous meso-tartaric acid and then boiling the filtered solution. The meso-tartrate comes down as a white granular precipitate. It is well washed with boiling water and dried over sulphuric acid in a desiccator for twenty-four hours. In this state it contains one molecule of water.

Scandium $\alpha\beta$ -Dibromopropionate,



I have not prepared either the normal or the basic dibromopropionate in a pure state, but I have obtained a salt corresponding to equimolecular proportions of the two salts, having the above composition. Scandium dibromopropionate is almost insoluble in hot or cold water, and when dried over sulphuric acid in a desiccator is a white amorphous powder, so extremely electrical that it requires great care in powdering and moving it from one vessel to another or it flies out of the mortar or watch-glasses.

Scandium Citrate,



is a dense white precipitate, soluble in excess of ammonium citrate solution.

Scandium Orthochlorobenzoate, $\text{C}_6\text{H}_4\text{ClCOOScO} + (\text{C}_6\text{H}_4\text{ClCOO})_2\text{Sc(OH)}$, forms a white amorphous precipitate, slightly soluble in hot water.

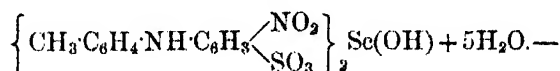
Scandium Metanitrobenzoate, $[\text{C}_6\text{H}_4(\text{NO}_2)\text{COO}]_3\text{Sc} + 4\text{H}_2\text{O}$.—Metanitrobenzoic acid is neutralised with ammonia, a hot solution of Scandium nitrate added till no more precipitate is formed, and the whole boiled for a few minutes. A white crystalline precipitate falls down. The metanitrobenzoate is very slightly soluble in water, and from a hot solution it separates in the form of flat crystals displaying brilliant colours when examined by polarised light.

The Scandia used in some of these experiments was intentionally not quite pure, being vitiated with a little yttria and ytterbia. On testing, the Scandia resulting from the decomposition of the metanitrobenzoate showed no trace of the dominant lines of yttrium or ytterbium, while the earth precipitated from the mother-liquors of the Scandium metanitrobenzoate on spectroscopic examination showed strong lines of both impurities. It will be remembered that Neish found that metanitrobenzoic acid was capable of separating thorium from its accompanying earths with quantitative accuracy. Further experiments with this acid are in progress.

Scandium Phthalate, $C_6H_4 \begin{smallmatrix} \diagup COO \\ \diagdown COO \end{smallmatrix} Sc(OH) + H_2O$.—When a solution of Scandium nitrate is added to a solution of ammonium phthalate, an amorphous white precipitate of Scandium phthalate comes down. It is slightly soluble in excess of Scandium nitrate, and insoluble in water or in excess of ammonium phthalate.

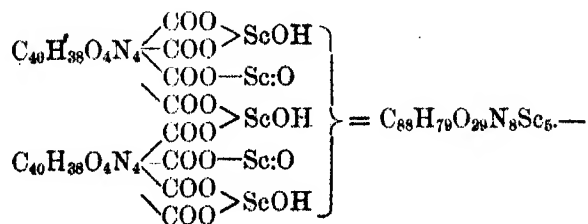
Scandium Tetrachlorophthalate, $C_6Cl_4 \begin{smallmatrix} \diagup COO \\ \diagdown COO \end{smallmatrix} Sc(OH) + 6H_2O$.—On mixing together equivalent proportions of Scandium nitrate and ammonium tetrachlorophthalate a dense white amorphous precipitate comes down, almost insoluble in hot or cold water. When washed and dried in the air, Scandium tetrachlorophthalate has the composition given above.

Scandium 2-Nitrophenyl-4'-tolylamine-4-sulphonate,



The sodium salt of this acid is dissolved in water and a solution added of Scandium nitrate. If the solutions are strong, a red precipitate falls; if weak, the mixture must be concentrated. On cooling, the Scandium salt separates in feathery crystals of a fine scarlet colour. It must be purified by re-crystallisation from a hot aqueous solution. The crystals are slightly soluble in cold water.

Scandium Octamethyltetraaminodihydroxyparadixanthylbenzenetetra-carboxylate,



By the kindness of Dr. Silberrad I have had an opportunity of experimenting with octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid.

Previous experiments would lead one to expect the Scandium salt of this acid to have the composition $C_{44}H_{40}O_{14}N_4Sc_2$. This I could not prepare, the salt produced by metathesis containing more Scandium than this formula admits of. The only Scandium salt I could form of this acid has the composition shown above.

Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid is a dark red powder, insoluble in water and easily soluble in dilute ammonia. The solution in ammonia, very slightly alkaline, is exactly neutralised with acetic acid; to the hot solution Scandium acetate is added and the whole boiled. On cooling, scandium octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylate comes down as a red powder, insoluble in cold water.

More than once I have been asked why I chose such very out-of-the-way acids wherewith to prepare Scandium salts? I give my chief reason:—Attempts on several occasions have been made to discover a means of separating some of the "rare earths" from their companions by forming compounds with weak organic acids. Thus, in 1897, Kosmann* employed citric acid in the separation of thoria. Urbain† used acetylacetonate of sodium for the same purpose. Metzger‡ tried maleic acid, cinnamic acid, picric acid, phthalic acid, and fumaric acid. He found fumaric acid effectual in separating thoria from the other earths in monazite, while the other acids also gave partial separations, although not complete.

In 1904, Neish§ tried many organic acids for the separation of the rare earths, chiefly thoria. Among other acids, he tried gallic, tannic, citric, salicylic, oleic, linoleic, paratoluic, oxyisophthalic, benzoic, meta-, ortho-, and para-nitrobenzoic, and fumaric. Of these, metanitrobenzoic acid proved most effectual, the process being capable of accurate quantitative results. It was found that other rare earths besides thoria behaved differently towards these acids, but the variation was not sufficient to enable the reactions to be used for accurate separations.

Soon after those experimental papers appeared I commenced similar researches hoping to find an organic reagent which would be a precipitant for some of the yttria earths—if not with quantitative accuracy, at all events

* 'Chem. Centralb.,' 1897, Part I., p. 837; 'Chemical News.,' vol. 86, p. 218.

† 'Bull. Soc. Chim.,' 1896, vol. 15, p. 347.

‡ 'Journ. Am. Chem. Soc.,' vol. 24, No. 10; 'Chemical News,' vol. 86, pp. 218, 229, 242.

§ *Ibid.*, vol. 26, No. 7; 'Chemical News,' vol. 90, pp. 196, 201.

with sufficient separation to allow a fractionation method to be based on the reaction. My results, not being sufficiently definite, were never published; but as the organic acids were in my laboratory when the Scandium research was commenced, I preferred to use these acids, of which the purity and the history were known, rather than start afresh with acids of unknown history.

On the Rotatory Character of some Terrestrial Magnetic Disturbances at Greenwich and on their Diurnal Distribution.

By ROBERT B. SANGSTER.

(Communicated by Dr. C. Chree, F.R.S. Received March 8,—Read April 28, 1910.)

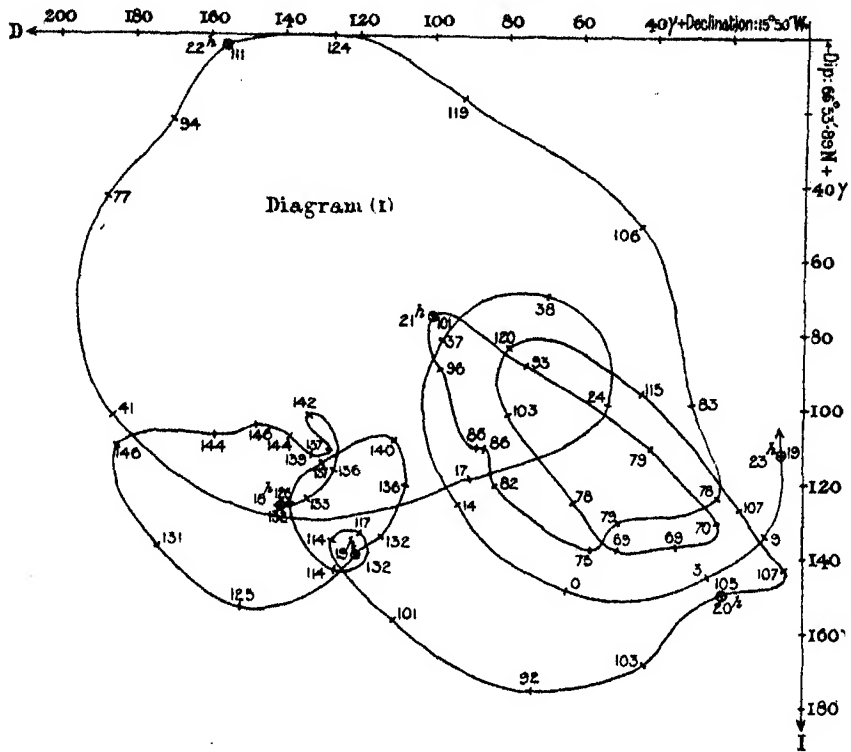
On the occasion of a brilliant display of aurora some apparently rotatory movements in the position of the corona suggested to the author the possible existence of similar changes of direction in the total magnetic force during disturbance. For investigating these changes the most convenient available data were the plates published with the "Greenwich Magnetical and Meteorological Observations" (hereafter referred to as the "Report"), showing on a reduced scale the diurnal registers of the three components of magnetic force for several disturbed days in each year. The eight years 1900–7 were dealt with, and a preliminary inspection of all the registers figured for these years was made to select an example for special consideration. The published registers are reduced in scale from the originals in the ratio 11 : 20, and to lessen the chance of error on this account, it was decided to select a disturbance showing comparatively slow, but steady and decided, changes. The registers selected in the first instance were those for October 12, 1903, and it was decided to determine the variation in direction of the total force from 18 hours onwards, at intervals of about 5 minutes, leaving out of account the effect of the small temperature variations recorded, for reasons presently to be stated. This variation in direction was found in terms of transverse deflecting force, the unit employed being 1×10^{-8} C.G.S. (1 γ).

In the following remarks the letters D, H, and Z denote the declination, the horizontal force, and the vertical force, respectively; F and I, respectively, denote the total force and the dip; while the prefix Δ signifies inequality increments. Ordinates of the components D, H, and Z were measured on the plate at time intervals of 1/40 inch, corresponding to a measure once

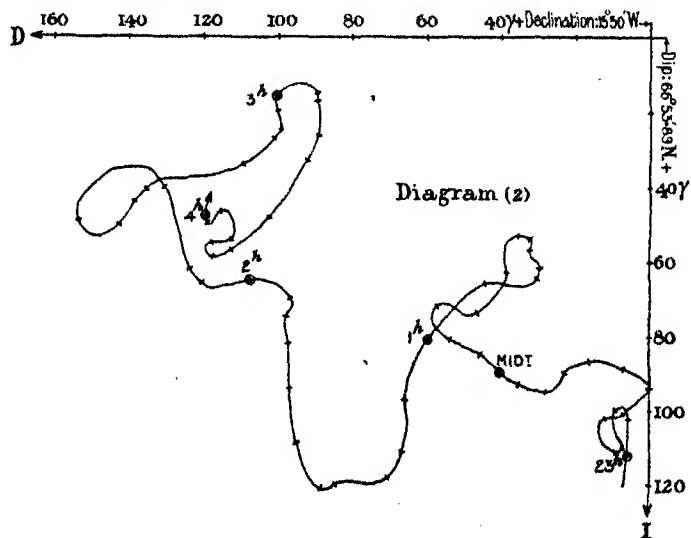
every 5 minutes, approximately. The zero of a scale divided to 1/40 inch was applied to the immediately preceding hour line, and points on the respective traces were thus set off at equal increments of time, and, from these, the force ordinates were measured to the adopted base lines. A division of the hour intervals into 12 equal parts was not so important as having the ordinates measured at exact time equivalents in all three registers. Regarding the accuracy with which the three registers were placed in time juxtaposition for the purpose of photo-lithographic reduction there is the assurance given in the "Report" (p. 37 for 1903) that great attention has been paid to this detail.

Values of ΔD were measured and tabulated directly in units of γ . This really represents the component ($H\Delta D$) causing variation in the direction of the total force transverse to the magnetic meridian. The component perpendicular to $H\Delta D$ and to the axis of the dipping needle is $F\Delta I$, causing variation in the angle of I in the magnetic meridian. Therefore, diurnal variation of the direction of the total force can be represented by rectangular co-ordinates corresponding to $H\Delta D$ and $F\Delta I$. For the determination of $F\Delta I$ base lines were drawn on the plate (III, 1903, October 12 and 13) at the scale marks representing $27 \times 10^{-3} H$ for the H trace and at $14 \times 10^{-3} Z$ for Z. The absolute values of the adopted base lines are, approximately, 18,500 γ and 43,610 γ , respectively, and ordinates at the stated time intervals were measured \pm from these, using the C.G.S. scales at the foot of the plate, in which one division = 10 γ . Values of $Z/H = \tan I$ were thus obtained, and thence ΔI and $F\Delta I$. In finding $F\Delta I$, F was taken as constant at 47,392 γ , and so 1' deflection in dip = 13.8 γ , nearly. Thus, values for describing Diagrams (1) and (2) were furnished, the former showing the variation in direction of the total force as viewed towards the N-seeking end of a freely suspended dipping needle for the hours 18 to 23, October 12, 1903, and the latter for the following five hours. Cross marks on the trace indicate the points of measured ordinates at simultaneous intervals of about five minutes, while the trace between is drawn with chief regard to the connecting up of the points in proper succession. By following the trace in Diagram (1) from 18 h. onwards, it will be seen that the movement is almost wholly rotatory in character and anti-clockwise in direction. The convolutions vary greatly in size and in time rate, but the long-continued levorotatory progression of the disturbance is very evident.

Doubt might naturally arise as to whether long stretches of trace joining up measured points in the diagram give a fair representation of the actual variation, e.g., from 22 h. 15 m. to 22 h. 20 m., and one might reasonably question whether there were not, in this case, an intermediate convolution,



perhaps of opposite rotatory character. Assurance on this point, however, is easily obtained from a consideration of the intermediate trend of the three traces in the Greenwich plate.



The author also assured himself that the effect on the diagram of applying the small and regular temperature corrections required to H and Z would be insignificant, and it was thus decided to neglect them.

Diagram (2) shows the disturbance to have continued in a changed character; there is a want of definiteness in the movements at times, but some of the changes after midnight are distinctly rotatory in a clockwise direction.

The total force ($Z/\sin I = F$) was also determined for each of the points in Diagram (1), and the values in γ 's of ΔF , taken all positive, are shown beside the corresponding points. An examination of these ΔF values indicated that the variations of the disturbance vector were, roughly, approximately in the horizontal plane, and a diagram showing the changes of force ΔD and ΔH was constructed and was found to be very similar in character to Diagram (1), the direction of all rotatory movements being the same in both.

This result obviously holds good so long as ΔH and ΔI are of opposite sign. But

$$\tan I = Z/H,$$

and so

$$\Delta I = \frac{1}{2} \sin 2I (\Delta Z/Z - \Delta H/H).$$

As $\sin 2I$ is positive, ΔI and ΔH are necessarily opposite in sign, unless $\Delta Z/Z$ has the same sign as and is numerically larger than $\Delta H/H$.

This did not occur in any of the seventy Greenwich disturbances dealt with here, and the nearest approach to it was found at 21 h. on November 15th, 1905, when the simultaneous changes were, approximately, $+80 \gamma$ in H and $+140 \gamma$ in Z. Therefore, subject to the above limitation, a rotatory effect in the horizontal plane implies a rotation in the same sense of the N-seeking end of a freely suspended magnet.

In order to determine the existence of rotatory movement in the disturbance vector it is usually unnecessary to measure force ordinates, for it is the time

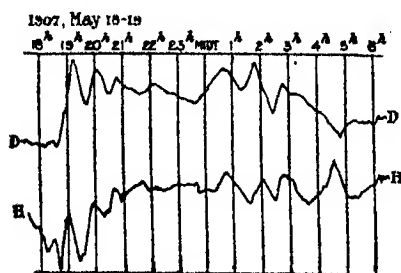


figure. Downward motion indicates increase of D and of H; increase of D means a movement of the disturbance vector to the west, or left, the observer being supposed to view the vector diagram from the south; increase

sequence of the changes of phase of the orthogonal components of the force in a plane which determines this feature. A good example of right and left rotations is furnished by a disturbance at Greenwich in 1907, May 18 d. 19 h. to 19 d. 5 h., the registers of which are reproduced on Plate IV. of the "Report" for that year, a copy of the reproduction being shown in the accompanying

of H means a movement of the vector to the north, or away from the observer. Referring then to the figure, just previous to 19 h. the vector is moving towards the south and to the right. A minute or two after 19 h., ΔH changes sign from $-$ to $+$ and the vector moves north, but still continues its motion to the right. The next change of sign occurs in D about 19 h. 15 m., when the vector changes from easterly to westerly movement, while still continuing its northerly course. Then H begins to decrease about 19 h. 25 m., and so the alternate changes of D and H continue in regular sequence to about 22 h., when the oscillation of H ceases. The motion of the disturbance vector here is clearly rotatory in character and anti-clockwise in direction. In the tabular statement of rotatory disturbances found later in this paper the disturbance figured is described as rotatory and negative from 19 h. to 21 h., and again in the half-hour preceding 22 h. But, next day, from before 1 h., continuously on to between 2 h. and 3 h., and again before 5 h., the rotatory movement is clockwise, or positive. At 1 h. the vector is moving to the left and north, it then changes to right hand and northerly motion at 1 h. 20 m., and to right-southerly motion at 1 h. 35 m., the same sequence continuing to 2 h. 30 m. Between 4 h. and 5 h. the same reasoning shows there was a large semi-circular movement of the vector in a clockwise direction.

It was apparent, therefore, that some magnetic disturbances resulted from more or less conical motion of the line of total force, some movements showing clockwise (positive) and others anti-clockwise (negative) change, and a consideration of cases already described shows the remarkable feature of the negative rotatory movements occurring before midnight and those with a positive or right-handed rotation after that hour. An orderly feature of the kind in the complex subject of magnetic disturbances would be a useful stepping stone for any general theory of the subject, and the cases quoted could not but rouse curiosity as to the existence of some regular diurnal distribution. A close scrutiny was therefore made of all the disturbed magnetic registers published with the "Reports" for the eight years 1900-7 to pick out all clear cases of rotatory change after the manner already described. Some cases of magnetic storms having very rapid changes of phase had to be omitted from consideration, owing to the uncertainty as to the relative epoch of these changes in the several components. Seventy-two sets of traces in all were dealt with, and the practice was to set down a $+$ or $-$ before or after the hour line according as positive or negative rotation was in evidence in the 30 minutes preceding or following the exact hour. One sign, counting as one, was tabulated whether there occurred but one half circle of rotation, or one complete circle, or more, as sometimes happened. In a few cases $+$ and $-$ rotations were found in the same half

The afternoon interval, during which no positive rotations appear, is extended in the individual seasons, in winter and equinox up to noon, in summer up to midnight.

[illegible]

Table II.—Equinoxes.

	NOON	13	14	15	16	17	18	19	20	21	22	23	MIDT	1	2	3	4	5	6	7	8	9	10	11	NOON	
1900 Mar. 8-9														++	++				-							
" " 8-10																++										
" " 15																			++							
1901 " 24-25														++	+					++						
" Sept 10-11																++	++	++								
" Oct. 6-9														++	++	++										
1903 Apr. 30-31																										
1903 Sept 19-20																			++	++	++		+	--	--	
" " 20-21																										
" Oct. 12-13																	+		+						-	
" " 13-14																	++	++	++							
" " 30-31																										
1904 Apr. 1																										
" " 15																	+		+		-	+			-	
" Sept 25														++			+	+		++	++					
" Oct. 21-22																			++	++						
1905 Mar. 2																										
" " 7																									++	
" Apr. 1																										
" " 2																										
1906 Sept 22-23																										
1907 Mar. 10-11																										
" " 11-12																										
" " 21-22																										
" Sept 10-11																										
" Oct. 15																										
" " 24																										
POSITIVES														2	3	3	4	5	6	6	5	4	5	5	3	1
NEGATIVES	1	2	2	1	3	2	2	6	6	6	6	10	11	6	5	7	10	6	2	1	1	2	1	1		

Table III.—Summer.

	NOON	13	14	15	16	17	18	19	20	21	22	23	MIDT	1	2	3	4	5	6	7	8	9	10	11	NOON
1900 May 5																									
1901 " 10																									
" July 12																									
1902 Aug. 21																									
1903 June 25-26																									
" Aug. 21-22																									
" " 22																									
1904 June 15-16																									
" July 6																									
" Aug. 3-4																									
1905 July 6																									
" Aug. 2																									
1906 " 7-8																									
1907 May 10-12																									
" " 20																									
" June 20																									
" July 10-11																									
" " 22-23																									
POSITIVES																									
NEGATIVES	1-1	2		1-1	2	2	2	3	3	3	4	2	5	4	5	1-1	1-1	1-1	3	4	3	1-1	2	1-1	2

Table IV.—All Seasons.

POSITIVES			I-2	I																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									</
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Table V.—All Seasons, in 1-hour intervals.

POSITIVES			5	1						4	6	9	14	24	19	19	15	12	2	5	5	2		
NEGATIVES	8	5	2	9	15	51	32	42	43	42	52	56	19	10	5	3	3	2	1			5	5	2

With regard to the interval from hour 6 to noon, Table IV shows a nearly clear separation of positives and negatives into equal periods; but the cases of rotation are too few here to do more than suggest that this

distribution may be general. It should be noted, however, that 6 h. 30 m. to 9 h. is the only period of the day showing an entire absence of negative rotations, while 12 hours later we find the greatest incidence of these, along with an entire absence of positive rotations.

*On the Direction of Motion of an Electron ejected from an Atom
by Ultra-Violet Light.*

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(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received March 25,—
Read June 2, 1910.)

When light is absorbed by matter it exerts, according to the electromagnetic theory of light, a pressure upon the matter, or gives a momentum to it, in the direction of propagation of the light. The existence of this pressure has been proved by a number of observers. When ultra-violet light is absorbed by matter we know that a part at least of the absorbed energy is expended in liberating cathode rays of small velocity. The momentum corresponding to the absorption of energy in this case thus probably appears in part in the form of moving electrons. We would, therefore, expect these cathode rays to have a component of velocity in the direction of propagation of the light.

The results that have been obtained in experiments on the secondary cathode radiation from substances exposed to γ - and X-rays also suggest that possibly such an effect exists. Thus the larger amount of secondary β radiation given off from the side of a radiating plate where the stream of exciting γ -rays emerges than where it enters has been explained by Prof. Bragg by supposing that the secondary β -rays are projected in the direction of propagation of the γ -rays. Cooksey showed that a similar effect exists with X-rays. It appeared a promising experiment therefore to look for such an effect in the case of ultra-violet light, and the writer accordingly carried out a set of measurements to test this point.

The apparatus by means of which the experiment was carried out is shown in fig. 1. The source of ultra-violet light was a vacuum tube A in which the discharge took place between an aluminium ring and an aluminium rod contained in a glass tube. It contained hydrogen at a pressure of a few millimetres. The electrodes were connected with the secondary circuit of an

induction coil whose primary circuit was connected with the 100 volts alternating electric light leads. Three Leyden jars were placed in the secondary circuit to increase the brightness of the discharge. A pencil of

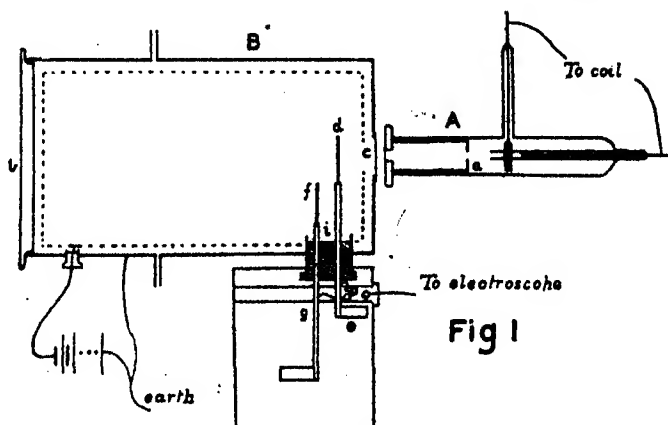


Fig 1

light was obtained by means of the stop *a*, the light leaving the tube by a circular thin quartz window 3 mm. in diameter at one end of the stop. The intensity of the pencil of light obtained was very constant.

B is a cylindrical brass chamber 8 cm. long and 7.5 cm. in diameter; it was closed at one end by a brass lid *b*, and the other end by a brass plate which had a circular quartz window *c*, 2 cm. in diameter, at the centre. Inside this chamber was another of the same shape but of wire gauze, the distance from the wire gauze to the inside surface of the brass chamber being about 0.5 cm. The inside wall of the chamber and the gauze were covered with lamp-black to increase their absorption of stray light and thus to reduce the amount of light reflected across the chamber. The chamber was earthed and the gauze usually connected to a high positive potential. The arrangement acted as a trap for the ions made near the surface of the chamber wall and the wire gauze by stray ultra-violet light; it is a better method than not using a gauze and having the chamber at a high positive potential to draw the cathode rays produced back into the metal.

A circular quartz plate *d*, about 0.3 mm. thick and 2.5 cm. in diameter, was mounted on a brass rod which passed through a brass tube mounted in an ebonite stopper *i*, so that the plate could be brought into the path of the beam of light or removed out of it as desired. The rod could also be rotated round its axis by means of the vane *e*. The quartz plate was covered on one side with a very thin film of platinum deposited on it from a platinum cathode in a discharge tube. Films of uniform thickness and of any desirable thinness can be obtained in this way.

The cathode radiation of the film under the action of ultra-violet light was investigated. An electric field was applied between the gauze and film in such a direction that the cathode radiation was pulled away from the film, the positive charge left behind being measured. It was of importance that the film should be very thin, so that the amount of cathode radiation corresponding to the amount of light absorbed might be as large as possible. The quartz plate did not show any appreciable change in appearance after the process of depositing the film till held over white paper, when it appeared just slightly darkened. The electrical conductivity of the film was tested and it was found that an electroscope could be charged practically instantaneously to any desired potential through the film. The surface of the other side of the plate was tested in the same way and found to insulate perfectly.

An aluminium plate *f*, covered on one side with two layers of gold leaf, was mounted on a rod *g* in the same way as the quartz plate. The rod slid freely in a brass tube mounted in the ebonite stopper *i*.

When the quartz plate was in the path of the beam of light and the rod *c* connected with the electroscope a large leak of positive electricity—about 10 divisions in 15 seconds—was obtained when the gauze was at a positive potential of 200 volts. But when the potential was reversed the leak was stopped. This shows that the platinum film emitted practically only negative particles under the action of the ultra-violet light, while the corresponding positive charge remained on the film; in the former case these negative particles were pulled away from the film, leaving it positively charged, and in the latter case they were driven back into the film. A very small fraction only of the leak was caused by the light reflected from the chamber walls. This was tested by measuring the leak with the quartz plate not in the beam of ultra-violet light, the leak being now solely caused by light reflected by the chamber walls and the gauze. The leak was found to have decreased to about 5 per cent. of the previous value.

A set of measurements was then carried out with the platinum film on the quartz plate facing the source of ultra-violet light, and with the film facing in the opposite direction, the plane of the plate being at right angles to the beam of light in each case. The plate *f*, by means of which the absorption of the light by the plate *d* was measured later, was moved out of the path of the beam of light and kept earthed. The potential of the gauze was always positive, usually from 200 to 600 volts. It was found that when the platinum film was facing away from the source of light the leak was about 15 per cent. larger than when the film was facing the light. Thus, for example, when the gauze was at a potential of 600 volts the leak in the former case was 20 divisions in 27.9 seconds, and in the latter case 20 divisions in 32.8 seconds.

gauze, and it was therefore raised to the same potential. The plate *f* was moved into the path of the beam of light and the rod *g* connected with the electroscope, while the rod *e* was kept earthed. The gauze was at a positive potential of 200 volts, and a leak was caused in the same way as before by the action of the light on the film of gold leaf on the plate *f*. Leaks were taken with the quartz plate in the path of the beam of light and with the beam unrestricted. When the platinum film was facing the source of light the ratio of the leaks was 0.541, this result being the mean of six readings. After an hour another set of readings was taken, which gave the value 0.553. The quartz plate was then turned round so that the platinum film was facing away from the source of light, and measurements carried out in the same way as before. The ratio deduced from the first set of measurements was 0.551, and another set of measurements carried out later gave 0.548. These results show that the same proportion of the beam of light is reflected by the quartz plate and film in the two cases. The intensity of the emerging light, it will be seen, is in both cases about 55 per cent. of that of the primary beam.

The results of the experiments may now be summed up as follows: Let us neglect the absorption of the light by the quartz plate. The amount of cathode radiation produced in the film would then be the same in the two positions of the quartz plate and film. We may then suppose that the film remained stationary, and measurements of the cathode radiation were carried out for both sides of the film. We then have that if we denote by unity the intensity of the light entering the film, the intensity of the light emerging at the other side is 0.55. And if the intensity of the cathode radiation on the side where the light enters is denoted by unity, the intensity of the radiation on the other side is 1.15. Now, if the electrons were ejected in all directions by the ultra-violet light, the cathode radiation on the emergence side, as already stated, should be smaller than that on the incidence side. The effect of the absorption of the light by the quartz plate in the actual experiments, it will be observed, is to decrease instead of increase this asymmetry. The experiments thus seem to show conclusively that the ejected electrons have a component of motion in the direction of propagation of the light.

Rubens and Ladenburg* have carried out some experiments on ultra-violet light, and obtained results which at first sight seem to indicate the existence of the above effect. These physicists did not undertake the experiments with the object of looking for the effect in question, and therefore do not draw any conclusions from their results relating to it. It will not be out of place, however, to investigate here whether some of their results have any connection with the subject.

* 'Berl. d. Deuts. Phys. Gesell.,' vol. 24, p. 749, 1907.

They passed a beam of ultra-violet light through different thicknesses of gold leaf to see whether the cathode radiation is a surface effect. Measurements of the intensity of the cathode radiation and that of the light emerging from or incident on the gold leaf were carried out for both sides of the leaf. The intensities of the incident and emergent pencils of light when one gold leaf was used were in the ratio of 1000 to 1, and the corresponding cathode radiations were in the ratio of 100 to 1. If the ratio of the intensity of the cathode radiation to that of the light incident on the leaf is denoted by unity, the ratio on the side where the light emerges will be 10. But this asymmetry does not show without further investigation that the cathode radiation is ejected in the direction of propagation of the light. The light as it passes through the gold leaf gradually decreases in intensity. The intensity of the cathode radiation at any point in the leaf will be proportional to the intensity of the light, and the intensity of the cathode radiation in the leaf thus gradually decreases as we pass from the side where the light enters to the other side. The ratio of the intensity of the cathode radiation at a point in the leaf to the intensity of the light falling on the leaf therefore decreases as we pass through the leaf in the direction of propagation of the light, while the ratio of the cathode radiation to the intensity of the light emerging from the leaf increases as we pass through the leaf in the opposite direction. Therefore, since according to Rubens and Ladenburg the cathode radiation emerging from the leaf is made up of radiation from all parts of the leaf, the ratio of the cathode radiation emerging from the leaf on the side on which the light falls to the intensity of the light should be smaller than the ratio of the intensity of the cathode radiation to that of the light emerging from the other side. To determine, then, whether this asymmetry shows that the ejected electrons move with the light requires some calculations to determine if the asymmetry is greater than it should be on the supposition that the electrons are ejected equally in all directions. These calculations would involve the coefficient of absorption of the cathode rays and that of the light, quantities whose magnitude is at present unknown. But when the cathode radiation on the side of a metal film where the light emerges is greater than that on the other side, as was the case in the writer's experiments, we have direct evidence that the cathode rays are ejected in the direction of propagation of the light. Rubens and Ladenburg's results cannot, therefore, as they stand, be said to constitute any evidence to show that the effect under discussion exists.

The result obtained in this paper is of interest in connection with the action of light on free electrons. From the nature of the results it seems reasonable to expect that a forward motion would also be given to an electron

when not associated with an atom on a wave of light passing over it. The experiments thus afford evidence in support of the theory that some of the free electrons which exist in the solar atmosphere, or in the atmosphere of any incandescent heavenly body, are driven into interstellar space by the light of the body. These streams of electrons are supposed by some physicists and astronomers to produce the aurora, and to give rise to the tail of comets.

I wish to thank Prof. Sir J. J. Thomson for his interest in these experiments.

[*April 22.*—After the foregoing paper had been written, it was suggested to the writer that the result obtained would appear more conclusive if the experiments had been carried out with the chamber exhausted to a high vacuum. Now, the ionisation of the air in the chamber by the ultra-violet light was negligible in comparison with the negative leak from the platinum film, as was shown by the complete absence of any leak when the gauze was raised to a negative potential. The only effect produced by the presence of the air is to impede the escape from the film of the negative particles which are produced by the light, so that a strong electric field had to be applied to produce a separation of the particles from the film. But the arrangement of the apparatus was such that the asymmetry in leaks observed could not in any way be due to this.

However, a set of experiments was now carried out with the chamber evacuated. The chamber was first exhausted down to about 2 cm. of mercury and the residual air absorbed by charcoal contained in a glass bulb which was placed in liquid air. The rod and tube joint was made air-tight by passing a tightly fitting rubber tube over it. The section of the aperture in the gauze through which the pencil of ultra-violet light entered the chamber was reduced in size, which had the effect of rendering the electric field more uniform at that part of the gauze. Observations were carried out with the gauze at a positive potential of 2 volts. When the film was facing the source of light it took the gold leaf of the electroscope 23.2 seconds on the average to move over five divisions of the scale, and when it was facing in the opposite direction the time was 20.2 seconds, which shows that the cathode radiation from the film is at least 14 per cent. greater in the latter case than in the former.

Another wire gauze was next placed in the chamber, parallel to the gauze with the aperture, so that the quartz plate was midway between these two gauzes. This was done in order that the electric field between gauze and

platinum film should be of the same intensity in each of the two different measurements. Joining the gauze to a positive potential of 4 volts, it was found that when the film was facing the source of light it took the leaf of the electroscope 36.5 seconds to move over 10 divisions of the scale, while it took 31.1 seconds when it was facing in the opposite direction. The negative leak from the film in the latter case is thus about 17 per cent. larger than in the former. The asymmetry in the leaks is slightly greater than that obtained before, owing to a different distribution of the electric field, the leak being not altogether independent of the intensity of the electric field even at the low vacuum obtained. In the former case the distribution of the field was such as to have a tendency to produce an asymmetry in the leaks of type opposite to the one observed.

When the gauze was raised to a negative potential practically no leak was observed. The results obtained thus support those obtained previously.]

On the Absorption of Gases by Charcoal.

By Miss I. F. HOMFRAY, D.Sc.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received April 4,—
Read May 5, 1910.)

The objects of the present research were: Firstly, to obtain accurate and systematic measurements, over as wide a range as possible, of the three variables in the charcoal-gas system, temperature, pressure, and volume of gas absorbed, for a number of different gases; secondly, to deduce therefrom some generalisations which should bring into line this mass of otherwise un-coordinated data; finally, to employ these relations, if justified by sufficiently wide applicability, to throw some light on the nature of the phenomena with which we are dealing.

The apparatus used was, essentially, a gas thermometer, the bulb containing 3 grammes of carefully purified cocoanut charcoal, connected with a mercury pump and gas burette. The dead space was found by calibration, and the actual volume of the gas-free charcoal by a separate series of experiments. Successive volumes of gas were admitted, and the pressures, up to 80 cm. of mercury, read at definite selected temperatures, ranging from that of boiling aniline to that of liquid air.

The volumes absorbed were calculated by difference, reduced to normal

temperature and pressure, and plotted on isothermals for each temperature. The gases employed were helium, argon, nitrogen, carbon monoxide, methane, ethylene, carbon dioxide, and oxygen, as well as mixtures of carbon monoxide and nitrogen. The series is thus typical of practically all varieties of chemical composition, and includes as wide a range of absorbability as is experimentally convenient. The absorption of helium is too small for the results to be used in subsequent calculations.

From the isothermal diagram, families of curves can be deduced to represent any relations which it may be desired to investigate, and each of these is a section of the three-dimensional figure which would be required to include the whole system. The fact that the curves are always homologous in all three planes, affords as good internal evidence of the reliability of the measurements as it is possible to obtain. Also, as the length of time allowed to elapse, after constant pressure had apparently been attained, varied considerably in different experiments, it seems probable, in view of the consistency of the results, that true equilibrium had, in all cases, been established.

From the isothermal and isobaric diagrams, points of equal absorption were read and curves plotted, having pressures as ordinates and absolute temperatures as abscissæ. The curves so obtained have been termed by Ostwald "isosteres," the absorbed volumes containing equal numbers of molecules in the gaseous state. No statement can be made as to the volumes under the varying conditions of the absorption measurements, and the term isochore is therefore not applicable.

The concentration by weight for each isostere is calculated in the form

$$C = \frac{w \times 100}{W + w},$$

where w = weight of gas absorbed in W grammes of charcoal, a finite value, $C = 100$, being thus obtained for the condition of gas or vapour in the absence of charcoal.

Two relations have been obtained which are valid, within experimental accuracy, for all the gases studied.

I.—At constant concentration—

$$\frac{T_0}{T_1} - \frac{T_0'}{T_1'} = R(T_0 - T_0'),$$

where T_1, T_1' , are the absolute temperatures read from any one isostere at any two pressures, T_0, T_0' , are the absolute temperatures at which any saturated vapour, which may be taken as standard, has the same pressures, and R is some constant. This is Ramsay and Young's rule for the relation

between the boiling points of two non-associated liquids. It is true also for the liquefied gases, these data being taken from the recognised sources. Ramsay and Young's law can be directly derived from Bertrand's vapour pressure formula

$$P = G \left(\frac{T - \alpha}{T} \right)^{50},$$

which also accurately expresses the isosteric curves, thus giving additional value to both expressions.

II.—At constant pressure—

$$-\frac{dT}{d \log C} = K.$$

The values have been mapped at pressures of 5, 30, 60 cm. for each gas, the agreement with the formula being very close.

Furthermore, in all cases at low pressures, and in the cases of argon and nitrogen at all pressures, when these straight lines are produced to $\log C = 2.0$, *i.e.* 100 per cent. concentration, each is found to intersect this ordinate at the independently found boiling-point of the liquefied gas at that pressure.

As examples of the utility of these two relations it may be mentioned that, by means of them, if the vapour-pressure curve of a liquefied gas is known, together with three values of temperature pressure and concentration in the presence of charcoal (*viz.*, one at about 5 cm. pressure and two at any single higher pressure) the whole absorption diagram can be mapped. This has been tested in the case of oxygen, where the number of measurements was small but sufficient to afford a thorough check of the method. The agreement with the independent experimental points was complete.

Again, the second relation affords a means of estimating the boiling point of liquid CO_2 at a degree of supercooling which is experimentally unrealisable. The straight line at $P = 5$ cm. for this gas cuts the line of 100 per cent. concentration at 148°A . From the law of corresponding states and the known critical temperature and pressure of CO_2 , the boiling point, 148°A ., at $P = 5$ is strikingly confirmed.

The actual values of $dT/d \log C$ for the different gases at the same pressure are interesting, inasmuch as they indicate a constitutional relation to a certain extent independent of the boiling points of the vapours, increasing uniformly with increasing complexity of molecular structure, from argon to ethylene, and following the same order as the molecular refractions and molecular volumes of the respective gases.

The isosteric curves, giving completely the change of pressure with

temperature at constant concentration, afford the means of calculating readily the molecular heat of absorption by the thermodynamical method

$$\lambda = \frac{d \ln P}{dT} 2 T^2.$$

The evaluation has been effected by a new and simple method based on Bertrand's formula, which has already been shown to be applicable to the absorption results.

From
$$P = G \left(\frac{T-a}{T} \right)^{50}$$

we obtain at once
$$\frac{d \ln P}{dT} = \frac{50a}{T(T-a)},$$

whence
$$\lambda = \frac{100 a T}{T-a},$$

the constant a being determinable from any two points on an isostere. This method is, of course, equally applicable to vapours.

In the case of CO_2 direct calorimetric measurements were made at atmospheric temperature. The charcoal bulb was surrounded with a large silvered vacuum vessel, successive small volumes of gas being admitted. The rise and subsequent fall of temperature was read on a Beckmann thermometer. Radiation corrections were made in the usual manner. The constant of the calorimeter was determined by substituting, for the charcoal bulb, a bulb containing a weighed quantity of water at the temperature of melting ice. After all corrections had been made, the mean of six very fairly concordant observations gave a heating effect of 3.2 calories for 10 c.c. of gas admitted. The value obtained by calculation is 3 calories, an agreement as close as can be expected, considering the numerous difficulties attending the measurement of such small effects.

A series of absorption measurements was also carried out with mixtures of CO and N_2 at the temperature of a paste of alcohol and solid carbon dioxide, *i.e.*, at 194.7°A , the curves for the separate gases having been previously determined. These two gases were selected as showing considerable difference of absorption and as having the same molecular weight.

The curve for the mixture at all compositions is found to lie between those for the single gases. In fact the distance of any point on the former from those on the N_2 and CO curves respectively, at the same pressure, is in the inverse ratio of their concentrations in the mixture. Thus the total volume is given by the equation

$$V = (vr + v'r')/100,$$

where v, v' are the volumes read from the N_2 and CO curves and r, r' the percentage composition of the mixture present. As the composition of the

separate phases was not determinable, the small unabsorbed volumes were not subtracted either for the mixture or the separate gases.

From the practical point of view it appears that this relation, in conjunction with the simple logarithmic formula already discussed, may be of considerable value in dealing with the separation of mixed gases by selective absorption in charcoal. For, by constructing the straight line diagram for a series of gases, we can determine by simple inspection the most favourable temperature and pressure under given conditions.

The pressure of a mixture of given composition and total volume can, of course, not be directly calculated from the partial pressures of the components, as the pressure-concentration curves are not straight lines; it can, however, be deduced by a graphical method.

The system is, therefore, completely determined by the four variables—temperature, pressure, percentage composition, and total concentration—as would be required by the phase-rule for a system having two phases, three components, and three degrees of freedom.

The question now arises, How far do the foregoing results throw any light on the nature of the absorption phenomena as a whole? The alternative hypotheses may be divided into three classes:—

(1) *Chemical Combination*.—No evidence of irreversible combination has been obtained in the course of the work hitherto described. At the conclusion of the experiments with oxygen, when the gas was pumped out the last fraction was analysed, but only a trace of CO_2 was obtained, CO being absent. Some measurements with mixtures of hydrogen and oxygen were also made at the same temperature as for CO and N_2 . The pressure rose steadily on addition of H_2 , the isothermal being a straight line and the hydrogen showing scarcely any absorption. There was thus no evidence of the formation of water. Entirely different results were obtained with NO. This gas reacts with charcoal at all temperatures, and there appears reason to believe that the combination is more complete at low than at high temperatures, as would be predicted from its endothermic character.

The reaction $2\text{NO} + \text{C} = \text{CO}_2 + \text{N}_2$ proceeds slowly, and the attempt was made, in conjunction with Dr. Gray, to investigate it quantitatively by pumping out and analysing the gases. The simultaneous partial absorption of varying volumes of the three gases, however, complicates the conditions so much that the progress of the presumably irreversible reaction could not be traced. The experiments have, therefore, not been published. About 50 per cent. of the NO was usually found to have been decomposed.

If, on the other hand, absorption were chiefly due to a temporary and reversible combination, it must be presumed that this would be reduced to

a minimum in the case of argon. A comparison of the curves for this gas with those for oxygen, for example, shows, however, that the differences are not at all of the order of magnitude to be expected, if chemical action of any kind were the determining factor. No evidence of molecular association has been obtained in the case of any of the gases.

(2) *Adsorption of Surface Condensation*.—This is the most generally accepted hypothesis. According to this view the very large volume of gas which charcoal is capable of retaining is attributed to the large surface exposed in the minute pores which perforate it and to the surface energy at the solid-gas boundary. This affords, however, no explanation of the radical difference exhibited by amorphous and crystalline bodies in this respect. For, whereas most amorphous bodies absorb water vapour and gases to a considerable extent, it has been shown by Theodore Richards that condensation of gases by finely powdered crystals is negligible, even on the scale of accuracy of his atomic weight determinations. The presence of liquefied gas, as such, in the capillary tubes of the charcoal can hardly be assumed at temperatures far above the critical points of the gases.

The thermal effect and temperature coefficient are also much greater than could reasonably be attributed to condensation on a large surface, the former being nearly three times the latent heat of the gas itself at its boiling point.

Apart from these difficulties, it does not appear to be possible to obtain the requisite data for testing directly Gibbs' surface-tension equation, for the charcoal-gas system and the logarithmic formulæ which are found to express the isothermals for the adsorption of iodine and dye-stuffs from solutions give quite unsatisfactory results when applied to the present experiments.

Also, if, in calculating the concentrations for each isostere, any other function of the quantity of charcoal, such as its surface area, were substituted for the mass, though the general form of the curves would be unchanged, and the isobaric straight-line relation (II) would hold, as far as the absorption results are concerned, all correspondence with the fixed points relating to the liquefied gases at $C = 100$ would be lost.

(3) The last hypothesis, that of solution, appears to offer the least difficulty and to agree best with the results of the present experiments. The term solution, taken in its broadest sense, implies molecular interpenetration and the formation of a single homogeneous phase in equilibrium with the undissolved gas phase.

The fundamental objection which has been raised against this hypothesis is that, as the pressure-concentration isothermals are not straight lines, the law of distribution between the two phases fails. Henry's law for the

solution of gases in liquids, however, only holds for concentrations very small compared with those with which we are dealing, and, in the case of helium, and other gases at high temperatures, the charcoal absorption isothermals are indistinguishable from straight lines up to absorptions of about 10 c.c. of gas in 3 grammes (roughly 2 c.c.) of charcoal.

Generally, however, there is no agreement with any of the laws relating to dilute solutions of solids in liquids, but there appears to be a very close analogy to concentrated solutions, as far as they have been investigated. Now, in dealing with solutions, the solvent, or component which is present in excess, is usually that with measurable vapour-pressure, the solute being the non-volatile component.

In the charcoal-gas system the conditions are reversed and are rather comparable to those of a moist amorphous precipitate, or of a solution from which nearly all the solvent has been removed by evaporation. In such cases considerable heat may be evolved on dilution and this "final heat of solution" is calculable from the expression $\frac{d \log P}{dT} RT^2$. This we have seen to be the case for the absorption of CO_2 .

Speranski has shown that Bertrand's formula expresses well the temperature-pressure relation for concentrated solutions of various salts and that the isothermals are not straight lines but, for moderate changes of concentration, fairly logarithmic curves. The heat of absorption has been calculated for a number of different concentrations and temperatures in the case of argon and is found to fall off rapidly with increasing gas concentration, towards the value of the latent heat of the liquified gas. At constant concentration the heat is almost independent of the temperature for low concentrations, the temperature coefficient increasing with increasing gas concentration. The value of $[\partial \lambda / \partial T]_c$ at 5 c.c. absorption is of the same order of magnitude as that found by Nernst for "ideal concentrated solutions" of H_2SO_4 in water. For such solutions, also, the molecular heat is fairly proportional to the change of boiling point for a small change of concentration of the non-volatile component.

This relation was, therefore, tested for the foregoing absorption measurements.

For simplicity, the calculations have been made for all the gases at the concentration $C = 1$.

The relation $-dT/d \log C = K$ then becomes $-dT/dC$ proportional to K .

Now let the concentration of the charcoal be C' , then for the moderate gas concentration when $C = 1$, dT/dC' is proportional to $-dT/dC$ and therefore also to K .

The following table gives the volumes of gas absorbed (A) and the values of T , λ and K at $C = 1$, $P = 5$; a is the constant of Bertrand's formula:—

	A.	a .	T.	λ .	K.	$\lambda/10K$.
N ₂	24.0	35.7	211.0	4270	75.0	5.7
A	16.8	33.6	213.5	3993	73.5	5.4
O ₂	21.0	42.7	221.0	5280	76.0	6.9
CO	24.0	40.0	227.0	4800	79.5	6.1
CH ₄	42.0	45.3	242.5	5570	81.5	6.8
CO ₂	15.2	55.4	318.0	6560	85.0	7.7
C ₂ H ₄	24.0	64.1	345.0	7800	106.0	6.8

The proportionality, though not complete, is certainly striking. It would be still more marked if calculated for concentrations less than 1 per cent., as here the temperature co-efficient of λ is already considerable.

There thus appears to be no fundamental objection to this hypothesis on thermodynamical grounds, and we have seen that the phase rule is applicable both for single gases and for mixtures, on the supposition that two homogeneous phases, gas and solution, are present. The charcoal is classed as a highly supercooled fluid, possessing the solvent properties of the fluid phase as distinguished from the crystalline, the presence of crystal faces and orientation apparently almost entirely preventing interpenetration by gases, liquids or non-isomorphous solids.

I have subsequently carried out some experiments on the absorption of CO₂ in para-azoxyphenetol, which is capable of existing in the crystalline and isotropic liquid phases. The absorption is found to be considerably greater in the latter phase, in spite of its higher temperature. The results will appear shortly.

On converting the amorphous charcoal to crystalline graphite, it entirely loses its absorptive power.

The chief claim of this hypothesis is, however, that it has suggested lines of investigation and methods of co-ordination of results, leaving a wide field for future research. It is intended to publish full experimental details in the 'Zeitschrift für Physikalische Chemie.'

My best thanks are due to Sir William Ramsay for the kind and helpful interest which he has taken in the work.

Flow of Water in Curved Pipes.

By JOHN EUSTICE, B.Sc., Professor of Engineering, Hartley University College, Southampton.

(Communicated by Sir J. Larmor, Sec. R.S. Received April 25,—Read June 2, 1910.)

Preliminary Experiments.—The author has for several years been engaged in experimentally investigating the resistance to the flow of fluids in metal pipes, both straight and curved. In order to study the effect of change of curvature, several experiments have been made on the flow of water in flexible pressure tubing with thick walls—a composite of rubber and canvas—the inner portion being red rubber surrounded by canvas, the canvas being covered on the outside with grey rubber.

Dimensions of tube:—Outside diameter 0·81 cm.; inside diameter 0·3684 cm. (calculated from the volume of the tube.)

A flexible tube was selected for the experiments because of the variation in the resistance to the flow of water in metal tubes which appear to be in the same surface condition; it was thought that if the same tube were used for a series of experiments at different curvatures this variation of resistance, due to the variation in roughness of the surfaces, would not occur. But another cause of difficulty was introduced, viz.: the slow recovery from strain of the rubber tubing, both after change of form due to coiling and after changes in pressure during the flow of water.

Two preliminary series of experiments were made, before the fuller investigation was undertaken. In the first series a pear-shaped glass vessel of 940 c.c. capacity was used as a containing vessel for the supply of water, the top being open to the atmosphere, and a short piece of tubing, about five times the area of the flexible tube, connected the latter to the containing vessel.

For straight-tube flow, the flexible tube was laid on an inclined plane; for coiled-tube flow, the tube was coiled around cylinders; but in all the experiments the angle of the helix was kept constant.

In the second series, practically the same arrangement was adopted except that a special containing vessel was employed which was designed so that the head of water was maintained constant throughout the series, and there was a glass connecting tube between the containing vessel and the experimental tube.

In the first series the time required for the flow of a known volume was recorded. In the second series, the quantity of water discharged in

200 seconds was recorded. In both series the water ran freely from the end of the tube into the measuring vessel. The method of experimenting was similar to that described on p. 110.

These experiments showed that the change from straight-tube flow to coiled-tube flow was accompanied by an increasing resistance, which when expressed in terms of time of flow and curvature, after correcting for diminution in the area of the tube due to coiling, could, for values of r/R between 0 and 0.06, be represented by an equation of the form

$$\{(t-t_0)/t_0\}^n = \theta R^{-1} = \text{constant} \times \text{curvature}.$$

Where t is time of flow in coiled tube,
 t_0 is time of flow in normal straight tube = a constant,
 r is radius of tube,
 R is radius of curvature of the coil,
 θ is constant for constant pressure-head,
 $n = 1.8$ nearly.

Extension of Experiments.—In the preliminary experiments the pressure-head on the water was nearly constant, and consequently the velocity of flow of the water was limited in range. In the fuller experiments now to be described the pressure-head could be varied and accurately adjusted so as to give velocities of flow both below and above the critical velocity; the change in the law of resistance to flow could thus be studied, when the flow changed from steady to unsteady motion in the straight tube and could be compared with the results obtained in the coiled tube.

The primary object of the investigation was to determine the variation in the resistance to the flow of water due to the curvature of the tube length, but as the area of the tube section diminished with an increase of curvature it was necessary to experiment separately on the effect produced on the flow of water in a straight tube by a variation in sectional form and area; hence two investigations were carried out, each consisting of several series of experiments.

A. *Coiled Tube.*—The determination of the combined effect of the variation in curvature of the length of the tube and of the form and area of section.

B. *Open Tube.*—The determination of the effect of the variation in the form of section of the straight tube.

Description of the Apparatus.—A cylindrical hydraulic tank has been erected in the hydraulics laboratory of the Hartley University College; the tank, which is 2 feet (61 cm.) diameter, gives a direct head of 36 feet (1,100 cm.) and is constructed so that arrangements can be made to increase the pressure by means of compressed air; the general arrangement is shown in fig. 1.

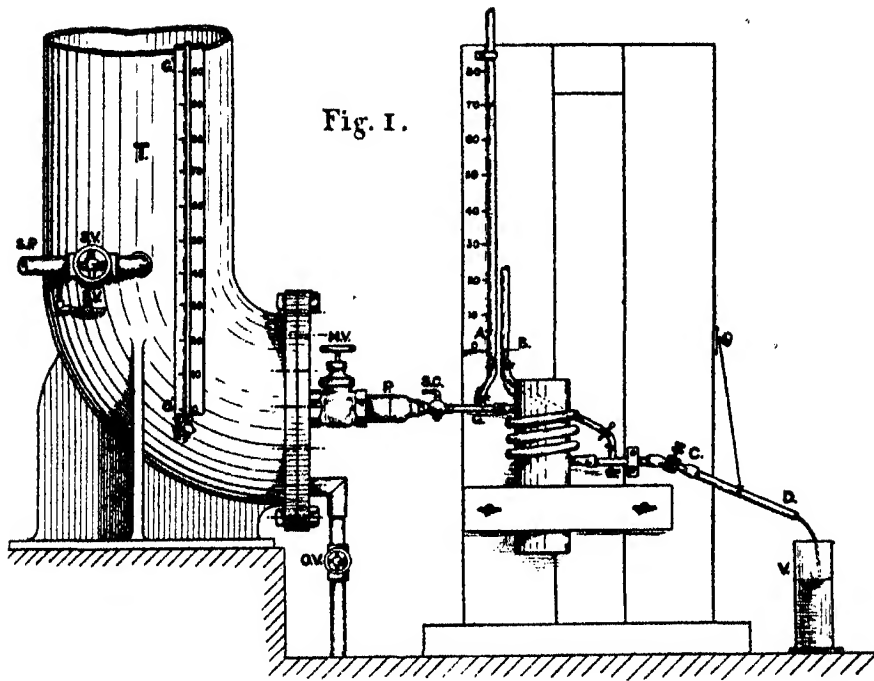


Fig. 1.

The supply of water to the tank T is taken from the town mains through a two-inch supply pipe S.P.; the flow of water into the tank is regulated by the supply valve S.V., while very fine adjustments of the level of the water in the tank can be made by the aid of a small by-pass valve B.V. which is fitted to the supply pipe. An outlet valve O.V. is provided for emptying the tank.

The head of water in the tank for its entire height can be read on gauge glasses G', G', attached to the tank. A short pipe P connects the tank with the experimental tube; between the stop-cock S.C. and the tank is the "full-way" main sluice valve M.V. In each experiment a brass gauge pipe G was screwed into the stop-cock S.C.; this pipe brought the flexible tube into communication with the tank.

A. Coiled Tube Experiments.—The arrangement adopted in the coiled tube experiments was as follows:—

Two brass pipes G, G, of the same bore as the flexible tube were attached to the ends of the tube, gauge holes (1 mm. diameter) drilled at right angles to the pipes communicated with the gauge glasses A and B, fig. 1.

The flexible tube was coiled around wooden cylinders which had been turned to the diameters necessary to give a whole number of coils for a given length of tube; the positions of the gauge portions G, G, could thus be the same in all the experiments. In each experiment the supporting cylinder

was fixed on a stand, the gauge portions of the tube were horizontal, and the gauges placed together as shown in the sketch.

The water in the gauge B (at the outlet end) was maintained at a constant level; the flow through the tube was regulated by means of a pinch-cock C. For fine adjustments of level the end of the drain tube D could be raised or lowered by a simple device; the loss of head between the gauges was given by the reading of the gauge A above the datum line at B.

For the lower pressures, up to a head of 200 cm., the loss of head was read directly in centimetres of water, above this head a specially constructed mercurial gauge was used.

Method of Experimenting.—The apparatus was set up and after allowing the water to flow through the tube for several minutes till the régime was found to become steady the inlet valve to the tank and the outlet pinch-cock C were adjusted until the required difference in the level was indicated by the gauges; when this difference became permanent the outlet water was caught in a vessel V, and the quantity discharged in a definite time (usually 100 seconds) was measured. The experiment was then repeated in the same way at other pressures until the series was completed.

A series was usually commenced at a low pressure, with a difference of head of a few millimetres, and continued under an increasing head until the difference of head was about 1000 cm.; in some of the experiments, however, the series was commenced with the pressure due to a full tank.

The experimental results obtained were tabulated as in columns (2), (5), and (6) of the accompanying Table I (No. 0c), which gives the results for the series when the tube rested on an inclined plane; the plotted results gave curves practically identical with the curves obtained on the same day with a straight tube in which both ends were kept at the same level. These experiments showed that the loss of head due to the changes from the horizontal to the inclined direction could be neglected; the standard of comparison was, however, that of the flow through the inclined tube 0c.

Table II (No. 10c) is a similar table for 10' coils. In column (7) a correction is made for temperature. This correction is based on Poiseuille's formula* for increase of flow with increase of temperature in a straight capillary tube; in the table it is assumed that Poiseuille's constants hold good for coiled-tube flow.

The coiled portion of the flexible tube was in all cases five-sixths of the length between the gauges, that is to say, one-sixth of the tube length was always joined on tangentially in the normal condition; the experimental values were corrected in the following manner.

* $Q \propto (1 + 0.03368 T + 0.000221 T^2)$, where T is temperature Centigrade.

Table I.—Inclined Tube. No. 0c.

Area of tube section, 0.1086 sq. cm.

Height of datum line from lower gauge pipe, 28.8 cm.

Distance between horizontal gauge pipes, 10.0 cm.

Length of tube between gauges, 97.8 cm.

Length of inclined part of tube, 81.5 cm.

(1) No.	(2) Head in cm. of water.	(3) Loss of head in horizontal part.	(4) (2)–(3) Loss in inclined part.	(5) c.c. per sec.	(6) Temp. Centigrade.	(7) c.c. per sec. for 14° C.
1	1.00	0.166	0.833	0.383	15.2	0.37
2	2.00	0.333	1.666	0.750	15.0	0.73
3	4.20	0.700	3.500	1.30	14.0	1.30
4	9.40	1.566	7.833	2.60	14.0	2.60
5	11.30	1.833	9.416	2.97	14.0	2.97
6	15.20	2.533	12.666	3.76	13.8	3.78
7	18.60	3.100	15.500	4.43	13.8	4.45
8	21.80	3.633	18.166	5.00	13.8	5.02
9	25.00	4.166	20.833	5.62	13.8	5.64
10	30.00	5.000	25.000	6.40	13.8	6.43
11	35.10	5.850	29.250	7.08	13.7	7.13
12	40.00	6.666	33.333	7.55	13.6	7.60
13	50.00	8.333	41.666	8.11	13.5	8.20
14	60.00	10.000	50.000	8.78	13.5	8.88
15	70.00	11.666	58.333	9.40	13.5	9.51
16	80.40	13.400	67.000	10.15	13.5	10.26
17	100.00	16.666	83.333	11.40	13.4	11.55
18	150.00	25.000	125.000	14.22	13.3	14.46
19	214.00	35.666	178.333	17.27	13.3	17.57
20	300.00	50.000	250.000	20.90	13.0	21.45
21	400.00	66.666	333.333	24.45	13.0	25.10
22	500.00	83.333	416.666	27.84	12.9	28.70
23	700.00	116.666	583.333	33.40	12.8	34.40
24	944.00	157.333	786.666	38.90	12.6	40.40

A compensating curve giving the loss of head for one-sixth of the pipe in its normal condition was plotted to a base line of discharge in cubic centimetres per second, the experimental readings in cubic centimetres per second were compared with the compensating curve, and the loss of head reduced by the amount given by the curve. The corrected values were taken as the loss in the coiled portion of the tube; this is shown in columns (3) and (4) of the tables.

Calibration of the Coiled Tube.—By means of a graduated burette attached to the tube the quantity of water required to fill the straight tube was determined, and also the quantity displaced at the various curvatures of the experiments; the area of the section corresponding to any particular curvature was calculated from the experimental data obtained.

The results are given in columns (1) to (4) of Table III, and the values of A/a are plotted on the curve aAA' in fig. 3.

Table II.—Ten Coils. No. 10c.

Area of tube section, 0.0735 sq. cm.

Diameter of coil : internal, 1.9 cm. ; external, 3.2 cm.

Height of datum line from lower gauge pipe, 28.8 cm.

Distance between horizontal gauge pipes, 10.0 cm.

Length of tube between gauges, 97.8 cm.

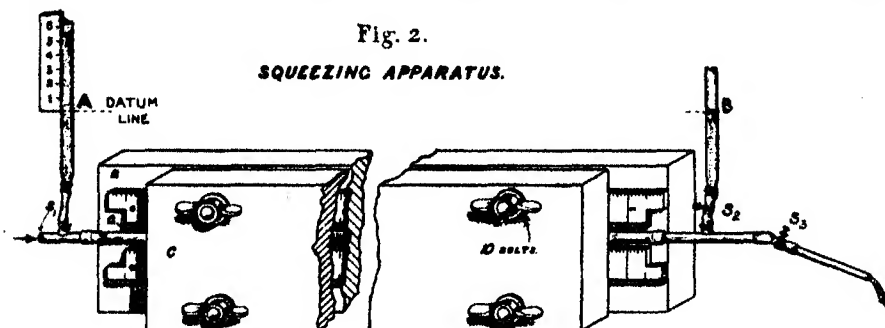
Length of coiled part of tube, 81.5 cm.

(1) No.	(2) Head in cm. of water.	(3) Loss of head in straight part.	(4) (2)–(3) Loss in coiled part.	(5) c.c. of water per sec.	(6) Temp. Centigrade.	(7) c.c. per sec. for 14° C.
1	1082.0	48.0	1034.0	20.94	13.2	21.40
2	966.0	42.5	923.5	19.72	13.2	20.16
3	857.0	37.5	819.5	18.53	13.2	18.92
4	780.0	32.0	698.0	16.94	13.2	17.31
5	585.0	24.5	560.5	14.80	13.3	15.10
6	448.0	18.1	429.9	12.60	13.6	12.73
7	330.0	12.3	317.7	10.34	13.8	10.40
8	237.0	8.0	229.0	8.32	14.0	8.32
9	186.5	5.3	181.2	7.15	14.1	7.10
10	120.0	3.3	116.7	5.24	14.2	5.21
11	93.5	2.6	90.9	4.40	14.2	4.38
12	72.4	2.1	70.3	3.70	14.5	3.65
13	47.8	1.45	46.35	2.75	14.7	2.70
14	29.65	0.97	28.68	1.93	14.9	1.88
15	16.6	0.58	16.02	1.23	15.0	1.20
16	7.9	0.28	7.62	0.68	15.5	0.654
17	5.89	0.21	5.68	0.532	15.6	0.510
18	2.38	0.08	2.3	0.248	16.0	0.233
19	1.45	0.05	1.4	0.160	16.1	0.150
20	0.53	0.02	0.51	0.0688	16.2	0.064

Table III.

(1) No. of coils.	(2) Curvature R^{-1} .	(3) Area A .	(4) A/a .	h/l average from		
				(5) 0.03 to 0.3.	(6) 0.3 to 3.0.	(7) 3.0 to 10.0.*
0	0.0	0.1066	1.0	n. 1.20	n. —	n. 1.81
$\frac{1}{4}$	0.0345	0.1066	1.0	1.31	1.55	—
1	0.0782	0.1066	0.999	1.30	1.50	1.90
2	0.1570	0.1057	0.990	1.34	1.51	1.89
3	0.2330	0.1047	0.982	1.35	1.49	1.78
4	0.3090	0.1025	0.962	1.36	1.48	1.80
5	0.3900	0.0996	0.934	1.36	1.48	1.74
6	0.4680	0.0960	0.900	1.35	1.46	1.73
7	0.5440	0.0907	0.850	1.32	1.45	1.74
8	0.6250	0.0850	0.796	1.31	1.44	1.66
9	0.7110	0.0790	0.741	1.29	1.42	1.63
10	0.7850	0.0735	0.689	1.23	1.41	1.67

B. Oval Straight Tube.—In order to study the effect of diminishing the area of section in the case of the straight tube a special form of squeezer was made (fig. 2), which consisted of two flat pieces of wood. In one of these,



the block B, a groove G was formed for the reception of the tube T; the cover C was bolted to B by 10 bolts, the effective depth of the groove being adjusted by the insertion of thin strips of rolled metal.

(a) Determination of the area of section.

The apparatus was set up in position, the tube being quite free in the groove, water was allowed to run until a constant *régime* was obtained, the ends of the tube and the outer gauge were then stopped by means of the stop-cocks at S_1 , S_2 , and S_3 , and a graduated tube was substituted for the upper gauge. The cover C was then screwed tightly against the block B, and the diminution in volume read in the graduated tube, the decrease in mean area being calculated from the data obtained. The results are given in Table IV.

(b) Loss of "head" at different velocities.

The same method of working was adopted as in the corresponding experiments on the coiled tube, *q.v.*

Table IV.

(1) Experiment mark.	(2) Area A. Experimental.	(3) A/a .	Values of n		Remarks.
			(4) Below C.V.	(5) Above C.V.	
A	0.1086	1.000	1.20	1.87	The reduction in area for D, E, F is beyond the limit of the experiments on the coiled tube. Compare the values of A/a in Column (3) with the values in Column (4) of Table III.
B	0.0882	0.826	1.08	1.92	
C	0.0735	0.688	1.08	1.93	
D	0.0637	0.597	1.08	1.94	
E	0.0550	0.515	1.04	1.86	
F	0.0516	0.483	1.12	1.58	

As in the coiled-tube experiments the part of the tube which was subjected to change of section was five-sixths of the total length of the tube, and corrections were made in the same way as is described on p. 111.

Results of the Experiments.—The results of all the experiments have been tabulated as in Tables I and II, and have been carefully plotted on squared paper. The curves which are reproduced in figs. 4 and 5 illustrate the method adopted.

In fig. 4 the abscissæ represent the quantities of flow in cubic centimetres per second (column (7) in Table I), the ordinates represent the losses of head in centimetres (column (4) in Table I). The curve *OaA* is for the straight tube (No. 0c, Table I). The curve *O1* is for the coiled tube (No. 1, one coil).

In fig. 5 the logarithms of the flow in cubic centimetres per second are plotted as abscissæ, and the logarithms of the loss of head as ordinates. The full line curve *OaA* is for the straight tube 0c. The other full line curves are for $\frac{1}{2}$, 1, 3, etc., coils. The dotted line curves *BB*, *CC*, *DD*, etc., are for the straight tube when it has been made oval in section by squeezing.

It will be seen from fig. 5 that for a given loss of head there is a very great increase in resistance, or diminution in the quantity of flow, as the number of coils increases, or as the curvature increases; the diminished flow, as is shown by the logarithmic curve, is most marked at points which are below the critical velocity in the straight tube. It may be noted, in passing, that there is no "critical velocity" region in the coiled tubes; but this and other peculiarities of these curves are dealt with below.

It has been shown that there is a reduction in area of the tube as the radius of the curvature decreases. But there is no appreciable reduction in area when the tube is slightly coiled as in "half coil" and "one coil," yet in these cases the diminution in flow is very great at discharges corresponding to the critical velocity in the straight tube; this is shown by the lines *OaA* and 1, 1 in fig. 5 and also in the corresponding diagram (fig. 4) for discharges between 5 and 10 c.c. per second.

Absence of "Critical Velocity" in the Coiled Tube.—In all the coiled-tube experiments the change in slope of the curves, as shown by the logarithmic plotting, is gradual. This change in slope is also seen in the values of n in columns (5), (6) and (7) of Table III, where n is the index of v in the formula $s = h/l = Kv^m/m$, s or h/l is the hydraulic gradient, v the velocity of flow, m the hydraulic mean radius, and K is a constant.

The difference in the character of the curves obtained for straight-tube flow and for coiled-tube flow is apparent in the two curves shown in fig. 4. This difference is even more marked in fig. 5, where *OaA* is plotted for a straight tube and *I.I* for the tube when formed into a coil of large radius, both tubes

Ratio of the Flow in a Coiled Tube to the Flow in a Straight Tube of the same Form and Area of Section.—In fig. 3 the abscissæ represent curvature R^{-1} . For a given hydraulic gradient the ordinate Ob represents unit quantity of water flowing through a normal straight tube; the ordinates of the dotted-line curve $bQ'q'$ represent the quantity of flow Q' through the tube when it is coiled; the ordinates of the full-line curve bQq represent the quantity of flow Q through the tube when it is straight; the time of flow is the same in each case. Corresponding to any given curvature R^{-1} , the cross-section of the tube both when coiled and when straight is of the same form, as well as of the same area A .

The lower curves $bQ'q'$, bQq , are for velocities of flow less than the critical velocity in the straight tube.

The upper curves $aQ'''q'''$, $aQ''q''$, are for velocities of flow greater than the critical velocity, and in the diagram the ordinates of the upper curves are drawn to twice the scale of the lower curves.

$xQ'/xQ = Q'/Q =$ flow in coiled tube \div flow in straight tube. Then $(Q - Q')/Q = \Delta Q/Q =$ loss of flow due to coiling \div flow in a straight tube of the same form and area as the coiled tube. And since Q varies directly as V (the velocity), the area being constant, $\Delta Q/Q = \Delta V/V =$ loss of velocity due to coiling \div velocity in a straight tube.

The ordinates of the curve OVv represent the ratio $\Delta Q/Q$ or $\Delta V/V$, for values of velocity below the critical velocity. $OV'v'$ is the corresponding curve for values of $\Delta V/V$ above the critical velocity.

These curves are represented by the equation $(\Delta V/V)^n = CR^{-1}$, where C is a constant for a constant hydraulic gradient.

The values of $\Delta V/V$ have been plotted for several hydraulic gradients; all the curves have the same general character, except that at velocities just above the higher critical velocity there is a change in the form of the curves near the origin, *i.e.* for small curvatures of the tube length.

The values of $\Delta V/V$ increase with increase of velocity up to the critical velocity, where a maximum is reached. At high velocities the form of the curves is the same as at low velocities, but the ratio $\Delta V/V$ diminishes with increase of velocity.

The value of n is 3 at the critical velocity, it becomes less than 2 just above the critical velocity, then increases to 3.3 at the higher velocities of the experiments.

Summary of Results.—The results of the experiments may be summarised as follows:—

(a) The flow in straight flexible tubes obeys the laws of flow in metal tubes as investigated by Prof. Osborne Reynolds ('Phil. Trans.,' 1883). In

Reynolds' experiments at velocities below the "critical velocity" the flow is proportional to the velocity. In the author's experiments the flow is proportional to the velocity raised to the power n ; when the tube was free, n varied from 1.18 to 1.2; when the tube was squeezed in a straight groove, n became 1.08 to 1.04. This discrepancy is accounted for in the foregoing investigation, for it is shown that a curvature of the tube length increases the value of n ; the flexible tube when not confined in a groove was sinuous, this sinuosity of the tube length increases n .

In other experiments on metal tubes, at velocities below the critical velocity, the author has found that whilst $n = 1$ for straight tubes, the effect of introducing angle bends in the tube length has been to increase n to 1.1.

The velocity at which the flow becomes turbulent occurs in the normal straight tube at the value given by Reynolds' formula

$$V_c = P/278 D, \quad P = (1 + 0.0336 T + 0.000221 T^2)^{-1},$$

where D is diameter of the tube in metres and T is temperature of the water.

The dotted curves in fig. 5 illustrate a peculiarity observed by Reynolds; it will be seen from the figure that the critical velocity region is different in the curves A, B, C, and F from the critical velocity region in D and E; the former were obtained from experiments at gradually increasing velocity, the latter at gradually decreasing velocity.

(b) The "critical velocity" region is present in all the squeezed tube experiments, even when the tube is flattened sufficiently to reduce the area to less than one-half the original area (as is shown by the set of curves A, B, C, D, E, F, in fig. 5). And the flow obeys the index law both below and above the critical velocity; that is to say, in the logarithmic plotting the lines below and above the critical velocity are both straight.

In all the coiled tube experiments, on the other hand, the value of the index n gradually increases with the velocity of flow, and there is an entire absence of the "critical velocity" region. The lines in the logarithmic plotting have a *gradually* increasing slope from the low velocities to the higher velocities of flow, as is shown by the set of curves in fig. 5.

The experiments show conclusively that this absence of the critical velocity region is not due to the variation in sectional form or area.

(c) The increased resistance expressed in terms of the loss in quantity discharged, or in loss of velocity for a given loss of pressure, is given approximately by the formula

$$(\Delta Q/Q)^n = (\Delta V/V)^n = CR^{-1}.$$

(d) The slow recovery of the flexible tube from the strain due to deformation caused by squeezing, or by coiling, adversely affected the

experiments ; but the results of the time lag were not sufficiently serious to affect materially the general deductions which have been made.

The author is continuing the investigation, in the hydraulics laboratory of the Hartley University College, with specially made metal tube of various forms of section, with the object of determining the commencement of turbulent flow in coiled tubes. He is also investigating the effect of the ratio of area to perimeter in oval tubes on the flow and critical velocity.

*The Effect of Pressure upon Arc Spectra. No. 3.—Silver ;
No. 4.—Gold.*

By W. G. DUFFIELD, D.Sc.

(Communicated by Prof. A. Schuster, F.R.S.)

(Abstract.)

No. 3.—SILVER. (Received January 9,—Read February 4, 1909.)

Further experiments upon the effect of pressure upon arc spectra have been made with the pressure cylinder (designed by Prof. J. E. Petavel, F.R.S.) which was employed by the writer in the investigations of the iron* and copper† arcs, in which an arc is formed between metal poles opposite a glass window through which the light is examined by means of the 21½ feet Rowland grating-spectroscope in the Physical Laboratories of the Manchester University. A system of mirrors allows the image of the arc, however unsteady it may be, to be kept almost continuously in focus upon the slit. Photographs of the silver arc in air have been taken under (total) pressures of 1, 6, 11, 21, 26, 41, 51, 61, 76, 81, 101, 121, and 201 atmospheres, and the results are given below for wave-lengths $\lambda\lambda$ 4000—4600.

A. General Features.

- I. The broadening of the lines with increased pressure.
- II. Their displacement towards the red end of the spectrum.
- III. The structure that becomes apparent in the wings of the strong lines under pressure.

* W. G. Duffield, 'Phil. Trans.,' 1908, A, vol. 208.

† W. G. Duffield, 'Phil. Trans.,' 1908, A, vol. 209.

- IV. The gradual disappearance of the line spectrum as the pressure is increased.
- V. Its replacement by a banded spectrum.
- VI. The development of the banded spectrum into a continuous spectrum.

B. *The Line Spectrum.*

I. *Broadening*—

Within the region $\lambda\lambda$ 4000—4600—

- 1. All silver lines broaden under pressure.
- 2. The broadening increases with the pressure; different amounts of exposure make it difficult to determine if the increase is continuous and linear with the pressure.
- 3. The broadening of the silver lines between $\lambda = 4000$ and $\lambda = 4600$ is unsymmetrical.
- 4. Under pressure, three types of broadening are distinguishable:—
 - i. The wings of the lines become hazy and band-like and present structure.
 - ii. The line broadens slightly, but preserves the character of a definite line.
 - iii. The line appears to become the violet edge of a band which stretches further towards the red as the pressure increases. The initial line ultimately ceases to be distinct.
- 5. No simple relation has been found between the original intensity of a line and its width under pressure.
- 6. The magnitude of the broadening of the first sub-series line is as great as 120 Å.U. at 20 atmospheres.
- 7. In lines of Type i, the structure is different for the two wings of the same line and also for different lines of the same type.

II. *Displacement*—

- 1. Under pressure the most intense portions of the silver lines which remain sufficiently definite for measurements to be made are displaced from the positions they occupy at one atmosphere.
- 2. Reversed as well as bright lines are displaced.
- 3. With increase of pressure the displacement is towards the red end of the spectrum within the region $\lambda\lambda$ 4000 to 4600 under consideration, but a few displacements towards the violet have been measured in another part of the silver spectrum.
- 4. The displacement is real and not due to unsymmetrical broadening.
- 5. The rates of increase of displacements with the pressure are different for different lines.

III. *Reversal*—

Within the region $\lambda\lambda$ 4000 to 4600—

1. Those lines that are originally reversed show signs of reversal up to 20 atmospheres, but at a later stage the disintegration of these lines masks any absorption that may take place.

2. The reversals become broader under pressure, but the structure of the wings of the lines makes this indefinite.

3. The reversals show two types, both of which are unsymmetrical.

4. In one type the absorbed part is on the violet, and in the other type on the red side of the centre of the bright line at one atmosphere.

IV. *Relative Intensity*—

1. The silver lines show marked changes in relative intensity under pressure.

2. Though their original intensities are extremely different they have all practically ceased to exist as lines at a pressure of 25 atmospheres.

3. The lines of the first sub-series are relatively the most weakened, first becoming, as in the case of copper, very broad diffuse bands, and ultimately being completely dissipated.

4. The line of the second sub-series vanishes without abnormal widening. It does not give rise to a diffuse band as do the first sub-series lines.

5. In these respects, in the limited regions of the spectrum examined in the two cases, the two subordinate series behave similarly in the silver and copper arcs.

C. *The Banded Spectrum.*

This spectrum, first noticeable at 20 atmospheres, is an emission spectrum.

I. *Broadening* :—

1. All the bands become broader as the pressure is increased.

2. It has not been determined if the broadening is continuous and linear with the pressure.

3. The broadening is, within the limits of the error of measurement, symmetrical.

4. The widths of the bands are very different, the largest measured being nearly 40 Å.U.; at 20 atmospheres they are seen to be composed of fairly fine lines.

II. *Displacement*—

The width of the bands makes the exact determination of their centres a matter of great difficulty, and it is impossible to say with certainty if there is any displacement as the pressure is increased. There is some slight evidence in favour of a small displacement towards the red.

III. *Reversal*—

None of the bands show any signs of reversal under pressure.

IV. *Relative Intensity*—

1. The bands further from the lines of the first sub-series gain in intensity as the pressure is increased relatively to those near these lines.
2. The absolute intensity of these bands also increases with the pressure, and less exposure is required at high pressures.
3. The banded spectrum is intimately related to the lines of the first sub-series.

D. *Brightness of the Arc.*

1. The brightness increases as the pressure increases.
2. Other conditions being equal, the brightness is dependent upon the freshness of the air in the cylinder, and also upon the coolness of the poles.

No. 4.—GOLD. (Received May 6,—Read June 9, 1910.)

The spectrum of the gold arc in air has been examined in the region $\lambda = 3550$ to $\lambda = 5100$ Å.U. under the following pressures:—5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 150, 175, 200 atmospheres (excess above one atmosphere).

I. *Broadening*—

1. All lines in the gold arc spectrum are broader under high pressures than when under atmospheric pressure.
2. The broadening increases with the pressure.
3. The broadening is different for different lines; some remain fairly fine throughout, others are greatly broadened, and others become so diffuse and hazy that they resemble bands at the highest pressures.
4. No fine structure such as was observed in the wings of the silver lines occurs in the gold arc.
5. Both symmetrical and unsymmetrical broadenings have been observed. The latter may be either unilateral or bilateral.
6. A few instances of a broadening towards the violet have been noted; in the majority of cases of unsymmetrical broadening the extension is greater on the red side.
7. Lines, whether symmetrical or unsymmetrical, broadened to the red or violet, preserve their type throughout the whole range of pressure.
8. In the case of some very strong lines two vibrating systems seem to enter into the composition of the broadened line, of which it is suggested that one is derived from the other by increased pressure.

II. Displacement—

1. Under pressure the most intense portions of those lines that broaden symmetrically or unsymmetrically towards the red are displaced from the positions they occupy at a pressure of one atmosphere, and the displacement is in the direction of greater wave-length.

2. Some doubt is felt about the sense and amount of the displacement of those lines that broaden towards the violet end of the spectrum; they appear to be displaced towards the violet, as are some of the silver lines, but the displacements are in such cases very small.

3. The displacements that have been measured are real and not due to unsymmetrical broadening, *i.e.*, the line is broadened about a displaced position.

4. Though the relation between the pressure and the displacement is approximately linear, there is evidence favouring a slightly greater rate of displacement at low than at high pressures.

5. The rates of displacement are different for different lines.

6. The lines of the gold arc spectrum can be grouped together according to their rates of displacement with the pressure.

7. Three groups can in this way be separated from one another, the displacements of Groups I, II, and III bearing to one another the approximate ratio of 1:2:4. A fourth group (Group IV) is formed by those lines that are broadened (and displaced?) to the violet.

8. The lines of Group III differ amongst themselves in the amounts of their displacement.

9. The displacements per atmosphere of the lines of Group III are approximately proportional to the cubes of their respective wave-lengths.

10. The highest mean displacement per atmosphere measured is 7.8 thousandths of an Å.U., the greatest individual displacement, at +200 atmospheres, being 1.26 Å.U.

III. Reversal—

None of the gold lines within the region examined showed any sign of reversal under pressure.

IV. Relative Intensity—

Changes in the relative intensities of lines occur under increased pressure. Lists are given of those lines that are weakened and strengthened under pressure.

V. Brightness—

1. The brightness of the gold arc increases greatly with the increase of pressure of the surrounding air.

2. The coolness of the poles and the freshness of the air supply are important features in causing the arc to burn steadily and brightly.

VI. *Banded Spectrum*—

Faint hazy patches of light appear upon the plates taken at the highest pressures in regions of the spectrum which at low pressures do not contain spectrum lines; they constitute an incipient banded spectrum resembling that observed in the silver spectrum at much lower pressures, but are not a marked characteristic of the spectrum and are not accompanied by a disappearance of the line spectrum as in the case of the silver arc.

Studies of the Processes Operative in Solutions. XI.—The Displacement of Salts from Solution by Various Precipitants.

By H. E. ARMSTRONG, F.R.S., and J. VARGAS EYRE, Ph.D.

(Received and read June 24, 1909.)

In a previous communication on this subject* we have described a series of observations made at 25° with ammonium, sodium and potassium chlorides and a few other haloids, the main result arrived at in the case of these chlorides being that the two precipitants, hydrogen chloride and ethylic alcohol, exercise the same kind of influence—a conclusion of some interest in view of the fact that alcohol is a neutral “unionisable” substance.

In all cases, the precipitant appeared to have an exceptionally marked effect when used in relatively small amount. The results obtained by Engel with hydrogen chloride at 0° also appeared to justify this conclusion.

As we could not but recognise that the determinations were subject to a variety of errors and that very small differences were involved in our estimations of the effect of small quantities of the precipitant, in extending the inquiry we have revised most of our earlier work.

We have used not only ethylic alcohol and hydrogen chloride but also methylic and propylic alcohols as precipitants of ammonium, potassium and sodium chlorides, both at 25° and 0°. A few observations have also been made on the influence of salts and of glucose as precipitants.

Speaking generally, the results serve to confirm most of the conclusions of our earlier work and even show closer agreement in the behaviour of the different precipitants than was formerly pictured; it is clear, however, that

* These Studies, Part II, ‘Roy. Soc. Proc.’ 1907, A, vol. 79, p. 564.

the effects produced by relatively small amounts of precipitant are not always so great as was supposed, especially in the case of hydrogen chloride, this conclusion being applicable to Engel's determinations made at 0° as well as to our own at 25° . The differences will be apparent on comparing the graphs now given (Diagram IV) with those published previously. We have satisfied ourselves that the earlier determinations, both our own and Engel's, were seriously affected by errors which we trust have been minimised in the present series of experiments.

The method followed has been that described in our previous communication, without material alteration. In operating at 0° , a rectangular glass tank, 36 cm. \times 30 cm. \times 30 cm., was used as the bath; this was charged with broken ice and water; by keeping the mixture constantly stirred, the temperature was easily maintained constant and very close to 0° C. during several hours. The tank was enclosed in a stout wooden box provided with a wooden cover, layers of felt being placed between the box and the tank. Small doors were provided—to take the place of the glass front of the tank used in determining solubilities at 25° —at opposite sides of the box, through which the solution could be viewed.

The salts used were prepared from the materials sold as "pure." As a rule, these were twice recrystallised from water; the hot, saturated solutions were cooled artificially and well stirred, so as to cause the substance to separate in fine crystals; to remove the mother liquor from these, they were centrifugalised in a perforated drum made of Berlin porcelain. The crystals were washed finally with alcohol and dried; the purified material was then sifted through rather coarse muslin which had been thoroughly washed. It should be mentioned that if the substance used be too fine, it is very difficult to prepare clear solutions. To purify sodium chloride, it was precipitated from a saturated solution by hydrogen chloride, then redissolved and reprecipitated, the subsequent treatment being that followed in the case of the other salts.

The alcohols were carefully dehydrated by means of lime and calcium turnings and fractionally distilled.

The extent to which individual determinations are in agreement is shown in the following table, in which the values given in Columns I and II are the results of separate experiments, A and B representing results obtained with two samples of the same liquid, the one withdrawn an hour later than the other.

The precaution was always taken to make duplicate determinations; when the two results were not in agreement, the experiment was discarded.

Table I.

Salt.	100 grammes of water dissolve at 25°.	
	I.	II.
Potassium chloride	grammes. A. 36·43 B. 36·40	grammes. A. 36·44 B. 36·37
Sodium chloride	A. 35·83 B. 35·71	A. 35·78 B. 35·77
Ammonium chloride	A. 39·50 B. 39·51	A. 39·52 B. 39·50

In Table II are given the apparent molecular hydration values deduced from a series of determinations in which the values arrived at are affected by what is probably the maximum experimental error.

Table II.

Salt.	Molecular proportion of precipitant per 1000 grammes water.	Apparent molecular hydration of precipitant.	
		I.	II.
KCl	¼ ethylic alcohol	A. 3·60 B. 3·80	A. 3·77 B. 3·60
NaNO ₃	¼ ethylic alcohol	A. 2·69 B. 2·72	A. 2·82
KNO ₃	¼ ethylic alcohol	A. 9·07 B. 9·01	A. 9·06

Relatively small variations of the solubility values affect the hydration values to a considerable extent. Experience has shown in the case of potassium chloride—of which several different samples were used—that it is necessary always to make use of the solubility value of each particular sample of salt in reducing the observations made with this salt; only when this precaution is adopted are the values deduced in satisfactory accordance. The particulars given in Table III relate to experiments in which one-quarter of a molecular proportion of precipitant per 1000 grammes of water was used; they are quoted as showing the character of the results arrived at in cases in which the experimental error exercises the maximum disturbing effect.

Table III.

Solubility value of KCl	35·97	36·27	36·37
Apparent molecular hydration of ethylic alcohol at 25°	A. 3·73 B. 3·45	A. 3·60 B. 3·80	A. 3·63 B. 3·76
Solubility value of KCl	35·93	36·37	
Apparent molecular hydration of HCl at 25°	A. 11·15 B. 11·00	A. 10·76 B. 11·04	
Solubility value of NaCl	36·08	36·19	
Apparent molecular hydration of HCl at 25°	A. 10·15 B. 9·95	A. 10·07 B. 9·90	

As showing the effect produced by substituting another solubility value for that of the particular sample used, the first result entered in the third column of Table III (3·60) may be taken, which is deduced from the solubility value 36·27; if the solubility value given in the second column, viz. 35·97, be substituted, the apparent molecular hydration values are reduced to 1·8 and 2·0 from 3·6 and 3·8 respectively. It is only in the case of potassium chloride that this necessity has arisen: it may be that the observed slight differences in solubility were due to the presence of impurity in some samples more than in others; we are inclined, however, to attribute them rather to differences in the state of division of the various samples.

The general consistency of the results arrived at with various salts and various precipitants may be regarded as proof that the practice we have followed is a legitimate one and that the results may be accepted as affording a generally accurate picture of the effects produced by precipitants. We do not pretend that they possess absolute value—this could only be if the experiments were carried out with all the refinements it is customary to lavish on determinations of atomic weight; but the end in view scarcely justifies the expenditure of so much time and labour on the inquiry, at all events until the main issues have been developed by a preliminary survey of the field.

The results arrived at are recorded in the following tables,* and in the Diagrams I to VI; in all cases the full line represents determinations made at 25° and the dotted line those made at 0°.

* [The seven tables now printed have been substituted for those originally submitted with the paper giving full details of the work, exception having been taken to their length: hence the delay in publication. In all cases the values given are means of two closely-accordant observations.—June 10, 1910.]

Solutes and temperature.	Concentration of precipitant.	Methylic alcohol.			Ethylic alcohol.			Propylic alcohol.		
		Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
NH_4Cl at 0° ...	—	298.40	5.59	—	298.40	5.59	—	298.40	5.59	—
	$\frac{1}{4}$	297.35	5.57	0.80	295.50	5.53	2.23	295.40	5.53	2.22
	$\frac{1}{2}$	296.55	5.55	0.75	291.95	5.47	2.38	291.30	5.45	2.62
	1	292.65	5.47	1.10	296.40	5.37	2.23	284.00	5.32	2.68
NH_4Cl at 25°	3	283.15	5.30	0.95	266.25	4.99	2.00			
	—	395.10	7.40	—				395.10	7.40	—
	$\frac{1}{4}$	394.75	7.39	0.19	Fide 'Roy. Soc. Proc., 1907, A, vol. 79, p. 567.			393.50	7.37	0.90
	$\frac{1}{2}$	393.85	7.37	0.35				390.80	7.32	1.21
NaCl at 0° ...	1	392.90	7.36	0.31				384.80	7.21	1.45
	3	386.20	7.23	0.41						
	—	357.75	6.13	—	359.65	6.16	—	357.75	6.13	—
	$\frac{1}{4}$	355.20	6.08	1.52	355.15	6.08	2.80	351.20	6.01	4.04
NaCl at 25° ...	$\frac{1}{2}$	(353.10)*	6.05	2.04	349.65	5.98	3.15	(345.55)*	5.91	4.37
	1	(347.45)*	5.95	1.88	337.80	5.79	3.37			
	3	—	—	—	301.60	5.18	3.00			
	—	362.95	6.20	—	Fide 'Roy. Soc. Proc., 1907, A, vol. 79, p. 567.			362.95	6.20	—
KCl at 0° ...	$\frac{1}{4}$	359.40	6.14	2.19				355.75	6.10	4.52
	$\frac{1}{2}$	357.60	6.11	1.65				350.20	6.00	3.92
	1	353.20	6.04	1.49						
	3	336.65	5.75	1.35						
KCl at 0° ...	—	283.55	3.81	—	285.15	3.80	—	283.55	3.81	—
	$\frac{1}{4}$	280.00	3.76	2.85	277.95	3.73	5.54	274.10	3.68	7.18
	$\frac{1}{2}$	276.35	3.71	2.83	271.10	3.64	5.47	265.45	3.56	7.10
	1	267.85	3.60	3.09	256.50	3.45	5.58	248.00	3.33	6.93
KCl at 25° ...	3	238.10	3.18	2.90	208.80	2.81	4.96			
	—	304.15	4.89	—				305.10	4.90	—
	$\frac{1}{4}$	361.90	4.86	2.00	Fide 'Roy. Soc. Proc., 1907, A, vol. 79, p. 567.			355.40	4.77	5.78
	$\frac{1}{2}$	357.10	4.79	2.12				347.70	4.67	5.30
KCl at 25° ...	1	348.70	4.67	2.34				331.50	4.45	5.06
	3	324.15	4.35	2.03						

* Solubility value, 359.65.

Hydrogen Chloride.

Solute.	Concentration of precipitant.	0°.			25°.		
		Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
NH ₄ Cl ...	—	298·40	5·59	—	395·10	7·40	—
	$\frac{1}{2}$	286·43	5·86	9·1	380·85	7·13	8·36
	$\frac{1}{4}$	271·23	5·08	10·17	366·00	6·85	8·25
	1	245·35	4·60	9·97	339·05	6·35	7·87
NaCl	—	357·75	6·13	—	360·80	6·18	—
	$\frac{1}{2}$	341·70	5·85	10·05	344·50	5·90	10·05
	$\frac{1}{4}$	324·45	5·50	10·44	329·05	5·64	9·88
	—	291·20	4·99	10·42	298·10	5·10	9·71
KCl	—	283·55	3·81	—	359·25	4·82	—
	$\frac{1}{2}$	267·25	3·59	12·96	341·55	4·59	11·07
	$\frac{1}{4}$	250·00	3·36	13·39	324·30	4·35	10·90
	1	(214·25)*	2·88	13·24	289·60	3·89	10·82

* Solubility value, 280·75.

Ethylic Alcohol.

Concentration of precipitant.	Solute, KBr at 0°.			Solute, NaNO ₂ at 25°.		
	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
—	536·75	4·51	—	920·30	10·83	—
$\frac{1}{2}$	529·25	4·45	3·14	908·80	10·70	2·82
$\frac{1}{4}$	502·85	4·22	4·66	896·60	10·54	2·89
1	491·75	4·13	4·65	870·95	10·24	2·99
2	455·25	3·82	4·22	825·35	9·70	2·86
	Solute, KNO ₃ at 25°.			Solute, K ₂ SO ₄ at 25°.		
	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
—	384·48	3·80	—	122·45	0·70	—
$\frac{1}{2}$	368·30	3·64	9·06			
$\frac{1}{4}$	354·40	3·50	8·68			
1	327·00	3·22	8·30	86·75	0·50	16·27

Potassium Nitrate.

Solute.	Concentration of precipitant.	0°.			25°.		
		Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
KCl	—	233·55	3·81	—	364·15	4·89	—
	$\frac{1}{4}$	284·25	3·81	—0·51	365·00	4·90	—0·52
	$\frac{1}{2}$	283·60	3·81	—0·01	361·65	4·86	+0·74
	1	287·60	3·86	—0·79	358·80	4·81	+0·80
	$1\frac{1}{2}$	—	—	—	355·20	4·77	+0·90

Sodium Nitrate.

Solute.	Concentration of precipitant.	0°.			25°.		
		Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
NaCl	—	359·65	6·16	—	362·95	6·20	—
	$\frac{1}{4}$	355·90	6·09	2·29	356·65	6·11	3·87
	$\frac{1}{2}$	351·20	6·02	2·61	352·30	6·03	3·27
	1	342·15	5·86	2·72	343·65	5·88	2·96
	2	—	—	—	325·50	5·58	2·87

Potassium Chloride at 25°.

Solute.	Concentration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
KNO ₃	—	384·48	3·80	—
	1	324·85	3·21	8·71

Glucose at 25°.

Concentration of precipitant.	Solute, KCl.			Solute, NaCl.		
	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.	Solubility in 1000 grammes of water.	Molecular solubility.	Molecular hydration of precipitant.
—	362·70	4·86	—	361·40	6·18	—
$\frac{1}{4}$	366·10	4·91	—2·10	364·15	6·22	—1·65
$\frac{1}{2}$	369·85	4·96	—2·15	364·80	6·23	—0·87
1	376·25	5·04	—2·08	369·90	6·32	—1·30
3	402·25	5·39	—2·01			

DIAGRAM I.

Methyl Alcohol as Precipitant.

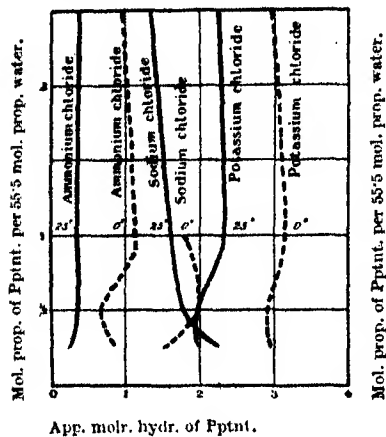


DIAGRAM II.

Ethyl Alcohol as Precipitant.

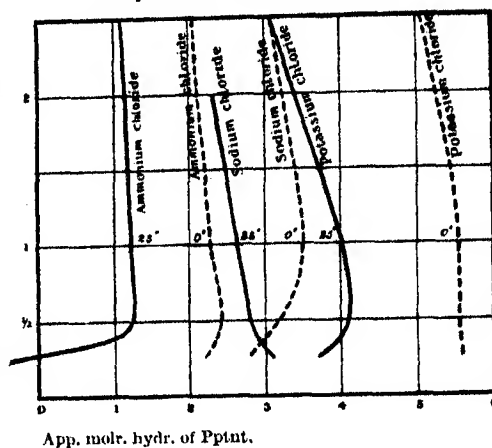


DIAGRAM III.

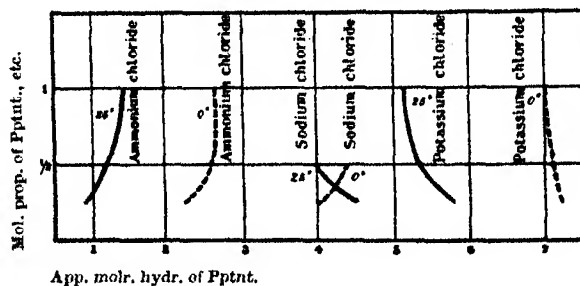
n-Propyl Alcohol as Precipitant.

DIAGRAM IV.

Hydrogen Chloride as Precipitant.

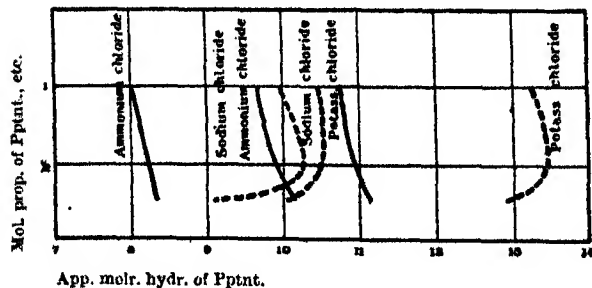


DIAGRAM V.
Various Precipitants.

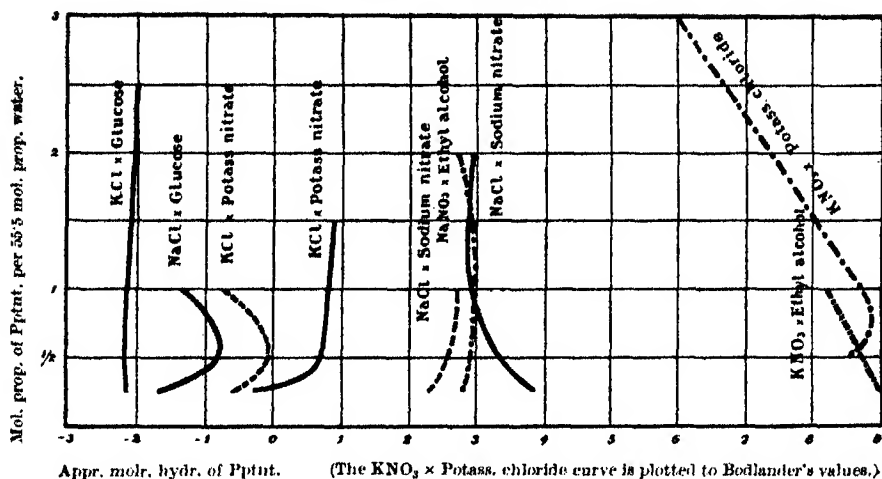
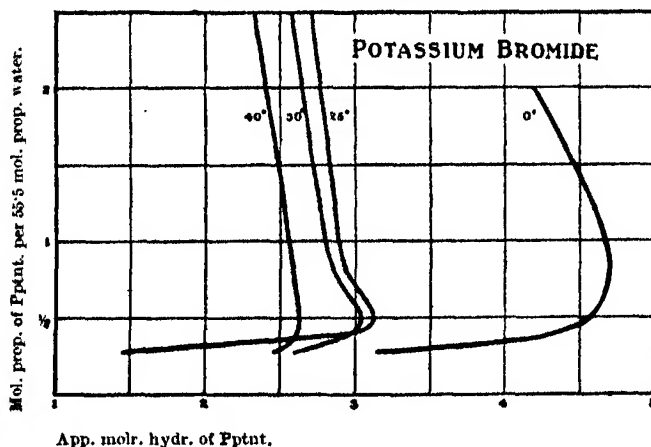


DIAGRAM VI.
Ethyl Alcohol as Precipitant.



As in the previous communication, the effect of the precipitant is expressed as if it were a dehydrating effect; in reality, however, our method of treatment involves merely an evaluation of the amount of water thrown out of action as solvent water by the precipitant. We were careful in our first account of the work to speak of the precipitant as controlling a certain amount of water and of the apparent molecular hydration of the precipitant, the main object in view was said to be to determine the relative concentrating effect of the precipitant in competition with that of the salt; and at the conclusion we insisted that it was necessary to recognise that the solvent itself, as well as

the substance in solution, is in a state of continued flux. It should not be possible to suppose that we ever regarded the results arrived at as true hydration values.

On reference to the relative positions of the graphs on the horizontal axes, it will be seen that, of the three alcohols, methylic is the least and propylic the most active precipitant. The activity of hydrogen chloride is considerably in excess of that of the alcohols. Of the three chlorides, ammonium chloride is least affected; next comes sodium chloride and then potassium chloride. In all cases, except when used in very small proportion, these precipitants are more effective at 0° than at 25° ; in the cases of ammonium and potassium chloride the two graphs are approximately parallel and somewhat distant from one another. In the case of sodium chloride, they are not only closer together but of contrary flexure and they intersect near the origin; it is clear that the behaviour of this chloride is peculiar.

The marked difference in the behaviour of the three alcohols is of great importance as throwing light on the precipitation process. It is very noteworthy that methylic alcohol has the least effect, although it is nearest to water, the most soluble and presumably, therefore, that which has the greatest attraction for water, whilst propylic alcohol, which is the least soluble and least attractive of water, has the greatest; the solubility of this latter alcohol is so slight that it cannot exist in the solution saturated with sodium chloride to a much greater extent than half a molecular proportion to 55.5 molecular proportions of water.

The extent to which the activity of the precipitants increases and their effect on the several salts in passing through the series of alcohols to hydrogen chloride, as shown by the position which the graphs occupy on the horizon on which the effect of a single molecular proportion of precipitant is indicated are given in the following table:—

	MeOH.	EtOH.	PrOH.	HCl.
NH ₄ Cl at 25°	0.4	1.2	1.5	8.0
0°	1.0	2.2	2.6	10.0
NaCl at 25°	1.6	2.5	3.7	9.7
0°	1.8	3.5	4.5	10.5
KCl at 25°	2.3	4.0	5.2	10.7
0°	3.2	5.5	7.0	13.3

To explain the effect produced by hydrogen chloride, which is so much greater than that of the other precipitants, it must obviously be assumed that this has a considerable direct dehydrating effect.

It is clear, however, that the precipitant does not act merely by attracting water to itself—the *condition* of the water must in some way be changed by the introduction of the precipitant, especially in the case of a substance such as propylic alcohol.

According to the hypothesis developed by one of us (compare No. VI of these Studies), the addition of any one of the precipitants to a solution would determine the dissociation of the water in the sense of the expression $(\text{H}_2\text{O})_n \rightarrow n\text{H}_2\text{O}$. Therefore the effect of adding a precipitant would be to increase the proportion of hydrone (H_2O) as well as of the other simpler molecules which are present in water, as such molecules would be more or less powerful dehydrating agents; in virtue of their tendency to polymerise and form water, they would condition the “dehydration” of hydrolated molecules of the solute and in this way would determine the separation of the substance from solution. This appears to be the most probable explanation of the manner in which the precipitant acts mechanically.

From this point of view, the greater effectiveness of the precipitant at 0° may be ascribed to the presence at this temperature of a larger proportion of more complex molecules in the water, that is to say, of a larger proportion of molecules which undergo simplification in the manner pictured; also to the presence of a larger proportion of complex, more easily precipitable salt molecules.

We have included in Diagram VI, representing the behaviour of potassium bromide in presence of ethylic alcohol, together with our own results at 0° and 25° , values deduced from Taylor's* results at 30° and 40° . It will be seen that his results are in complete harmony with ours. The gradual diminution in activity of the precipitant and the disappearance of backward flexure in the graphs, as the temperature rises, would seem to be clear evidence of a corresponding diminution in the proportion of hydrolated salt molecules.

That the condition of the water is disturbed there can be practically no doubt, as propylic alcohol has so much greater an effect than either of the other alcohols, both of which certainly have a greater affinity for water. That the condition of the salt in solution is also altered would seem to follow from the fact that, as shown in the following table, the apparent molecular conductivity of the salt is much reduced by the addition of an alcohol to the liquid: it will be noticed, moreover, that there is a striking similarity in the extent to which each of the three alcohols reduces conductivity on the one hand and solubility on the other. The difference in the condition of the solutions at 25° and 0° is also indicated, as well as the fact that a considerably greater effect is produced at 0° than at 25° .

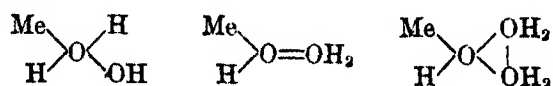
* ‘Journ. Phys. Chem., Cornell,’ 1897, vol. 1, p. 724. (cf. ‘Seidell's Solubilities,’ p. 237.

The values refer to solutions containing gramme molecular proportions of the materials in 1000 grammes of water.

Molecular Conductivities.*

	25°.	Reduction.	0°.	Reduction.
		Per cent.		Per cent.
KCl	112.30	—	65.35	—
+ MeOH	104.78	6.8	59.45	9.0
+ EtOH	98.47	12.3	54.74	16.2
+ PrOH	93.87	16.5	51.15	21.7
+ iPrOH	102.33	8.9	57.51	12.0
NH ₄ Cl	112.24	—	64.86	—
+ MeOH	104.74	6.7	59.22	8.7
+ EtOH	98.54	12.2	54.26	16.3
+ PrOH	93.74	16.5	50.40	22.5
NaCl	86.38	—	47.64	—
+ MeOH	80.55	6.7	43.36	9.0
+ EtOH	75.85	12.1	39.72	16.6
+ PrOH	72.17	16.4	36.62	22.7
+ iso-PrOH	71.70	16.9	36.62	23.1

To understand the difference in the effects produced by the several alcohols, it is necessary to consider what may be the condition of these substances in solution. It is improbable that they exist to any extent in an associated state—at all events in the more dilute solutions; to some extent, perhaps to a considerable extent, in the case of propylic alcohol, they may be present as simple molecules unattached to hydrone. A certain proportion of the molecules are doubtless associated with hydrone molecules in various ways—some being hydrolated, some simply hydronated and others poly-hydronated, thus:



The further removed the alcohols are from hydrone, the less such complexes will be likely to simulate the behaviour of corresponding molecules in water itself. From this point of view it is easy to understand that methylic alcohol has little effect on ammonium chloride, behaving almost as water, whilst propylic alcohol has a marked effect.

Similar considerations are applicable to salts. Salts such as we have dealt

* We are indebted for these values to Mr. D. Crothers. It may be mentioned here that, in making the determinations, he availed himself of a great improvement in the conductivity apparatus effected under the advice of Prof. T. Mather, F.R.S.; this consists in substituting a vibration galvanometer the latter had devised for the telephone which it is customary to use.

with are present in solution probably to but a small extent in an "unhydrated" state, either as monads or in more complex molecular states; the majority are in association with hydrone in various ways, either hydrolated or hydronated in simple or complex ways. The displacement of haloids such as we have studied from solution may be regarded as a consequence of the dehydration and dehydronation of such molecules, whether derived from monadic or polymerised molecules of the salt.

Our results appear to indicate that precipitants have but relatively little tendency to dissociate the complex salt molecules; if they had this effect to any considerable extent, the solubility of the salt would be increased rather than diminished. The increased solubility of potassium chloride in presence of potassium nitrate (Diagram V) is probably a case of this kind—the fact that the greater effect is produced at the higher temperature is in harmony with this explanation and affords an argument unfavourable to the conclusion that the two salts combine. The increased solubility of potassium and sodium chloride in presence of glucose, however, is perhaps due to the formation of a compound of salt with sugar.

It is noticeable that the graphs, in all cases, show a slight backward trend in their upper course. We are less inclined than we were formerly to regard this as due to the solvent action of the precipitant; we think that it is at least mainly a consequence of the production of a larger proportion of more soluble simplified molecules of the salt as the amount of the precipitant is increased.

Attention may be called to the various graphs relating to nitrates in Diagram V; the greater "sensitiveness" of nitrates is clearly indicated. The results are in accordance with the view which is generally held that nitrates have less affinity for water than chlorides.

The fact that sodium nitrate is less precipitable than the potassium salt is in agreement with the known greater tendency of the former to "assimilate" water. The similarity in the effect produced on potassium nitrate by ethylic alcohol and by potassium chloride (from values determined by Bodlander*) is again an illustration of our contention that no distinction can be drawn between electrolytes and non-electrolytes as precipitants.

It remains to consider the somewhat peculiar behaviour of sodium chloride. The inferior effect produced by small amounts of precipitant at 0° may be a consequence of the greater stability at this temperature of the "hydrated" salt complexes; the superior effect produced at 25° may be attributed, on the other hand, to the lessened stability of these complexes at the higher temperature. Evidently the salt is in a state of delicate

* 'Z. ph. Chem.,' 1891, vol. 7, p. 359.

balance in saturated solutions at temperatures not far removed from 0° between 0° and 25° .

In conclusion, it may be desirable again to emphasise our view that the phenomena of competitive dissolution are of a very complex character. It would seem probable, however, that the precipitation of salts from solution is mainly due to what may be termed collectively "*dehydration changes*," conditioned not only by the direct withdrawal of water from the solution by the precipitant but, in the case of neutral solvents particularly, also by the agency of the increased proportion of hydrone molecules brought into being in the water by the mechanical interposition of the molecules of the precipitant.

We desire to express our particular thanks to Mr. D. R. Keller, who with unwearied perseverance and care has carried out much of the practical work described in this communication, thereby rendering us invaluable assistance.

The Distribution of Velocity in the β -Rays from a Radioactive Substance.

By J. A. GRAY, B.Sc., 1851 Exhibition Scholar, University of Melbourne.

(Communicated by Prof. E. Rutherford, F.R.S. Received May 6,—Read June 9, 1910.)

[PLATE I.]

It is well known* that the α -particles emitted from a thin film of radioactive matter of one kind are initially projected at an identical speed. No definite evidence, however, has yet been obtained whether a similar result holds for a substance which emits β -particles in its transformation. Hahn has found by the electrical method that β -rays from a simple radioactive substance are absorbed very nearly according to an exponential law, and has utilised this property to decide whether the source of β -rays consists of one or more products emitting β -particles. This method, in the hands of Hahn and Meitner, has proved very fruitful in bringing to light new and unsuspected β -ray products.* In addition, it has been assumed by many

* Hahn and Meitner, 'Phys. Zeit.', 1909, p. 697.

writers that the exponential law of absorption is a proof that the rays are homogeneous, *i.e.*, that the β -particles are emitted initially at an identical speed, and, further, that the velocity of the β -particles does not change appreciably in traversing matter.

W. Wilson* has attacked this question from another direction. Using radium emanation, he has sorted out the rays from the active deposit by means of a magnetic field, and obtained rays which, if not homogeneous, only cover a small range in velocities. Testing these rays by means of an electroscope, he found that when the ionisation was plotted against the thickness of absorbing matter, the curve obtained was not exponential, but very nearly a straight line. This indicated that the absorption of nearly homogeneous rays was not a constant, but increased with the thickness of matter traversed. Such a result can only be explained by a loss of velocity in β -rays as they pass through matter. It shows also that an exponential law of absorption does not signify homogeneous β -rays, but rather rays with a particular distribution of velocities.

This point of view has been a matter of discussion between Hahn and Meitner† and Wilson‡ and the former in their paper supported the view that an exponential law of absorption is a proof that the β -particles are homogeneous, and do not decrease appreciably in velocity in passing through matter. It has been the object of the experiments described in this paper to obtain independent evidence on this important question by deflecting the β -rays from some radioactive substance in a magnetic field.

The photographic method was used, the detection of one or more sets of homogeneous β -rays being attempted. Radium emanation was the substance first used. The emanation produces RaB and RaC, both β -ray products, and when radioactive equilibrium is established we have a source of β -radiation which is approximately constant during the course of a few hours. The emanation was contained in a narrow thin-walled tube, similar to the tubes used by Rutherford and Royds when they proved that the α -particles were positively charged atoms of helium. The thickness of the tubes was such that it was equivalent to about 3.5 cm. of air, so that the α -particles from RaA and the emanation could escape. The tubes were made thin, so that there should be as little absorption as possible of the β -rays affecting the photographic film used, but enough thin black paper was placed over the tube to protect the film from the α -particles and the phosphorescence caused by them. Thus the β -rays had very little matter to pass through, so

* Wilson, 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 612.

† Hahn and Meitner, 'Phys. Zeit.,' 1909, p. 948.

‡ Wilson, 'Phys. Zeit.,' 1910, p. 101.

that if there were sets of homogeneous rays in the β -radiation, these should have been detected, even if the β -rays did change slightly in velocity in passing through matter.

The capillary tubing was joined to a vessel containing purified emanation, and the latter was pushed into the thin tube by mercury. The capillary tube was sealed off and placed in a lead tube fixed to the brass plate LM (Plate 1, fig. 1).

Fig. 2 represents the experimental arrangements adopted, the section being perpendicular to the tube in fig. 1. The apparatus was in the form of a box 12.5 cm. cube. The active material A was parallel to a slit S, 5 mm. wide, formed by two lead plates 1.3 mm. thick. A photographic film P could be fixed across the slit by means of the holder H. This holder fitted tightly into an opening in the box, which could be made air-tight. By means of the tube T connection could be made with a Fleuss pump in order to evacuate the box. The box was placed between the poles of an electromagnet, the magnetic field being parallel to the slit. When the film was placed in position, the box was evacuated and the photograph taken.

Several photographs were taken, but there was no sign of a set or sets of homogeneous β -rays. This can be seen from fig. 3. The narrow band is caused by the undeflected β -rays, in absence of a magnetic field. The other band, or magnetic spectrum, as it may be called, shows no sign of bands, the spectrum being quite continuous. The experiments, therefore, gave no evidence that there were sets of homogeneous β -rays emitted by RaB and RaC. The result, however, is confused by the fact that there are several β -ray products, and a more definite result would be obtained if we examined a substance in which there is only one element emitting β -rays. This was done by using RaE.*

As many experimenters have shown, the absorption of the β -rays of RaE is very nearly exponential over a wide range, and consequently, by taking photographs as above, we can easily see whether an exponential law of absorption signifies homogeneous β -rays or not. Some carefully purified RaD, which subsequent γ -ray measurements showed to be practically free from radium, was placed in a narrow groove in an aluminium plate. The groove was 0.4 mm. wide and deep and 1.3 cm. long. RaD, on disintegration, forms RaE and, when radioactive equilibrium is established, we have a practically constant source of β -radiation. A thick layer was necessary in order to

* The experiments of Antonoff ('Phil. Mag.,' vol. 19, p. 825, June, 1910) show that there is only one radioactive product between RaD and RaF, viz., RaE, which emits β -rays absorbed according to an exponential law. Formerly, two products, RaE₁ and RaE₂, were supposed to exist.

obtain photographs in a reasonable time, but as, on examination, the rays used were absorbed exponentially until the intensity was about 10 per cent. of the original intensity, this did not affect the result.

The absorption was tested in two ways. In the first the active material was placed about 10 cm. below a small electroscope and an absorption curve taken. In the other a small proportion of the rays were allowed to pass through a small hole in a lead screen and the absorption curve taken, using an ordinary β -ray electroscope. The absorption in both cases was practically exponential over the greater portion of the range, being somewhat greater after the intensity had been diminished to 10 per cent. Curve A, fig. 4, in which the logarithm of the activity is plotted against the number of absorbing sheets, is practically a straight line. The average thickness of a sheet was 0.0848 mm., the value of the absorption coefficient obtained being $\lambda = 43.1 \text{ cm.}^{-1}$. The tube A of fig. 1 was replaced by the aluminium plate, and the slit S was formed by two graphite plates 1.4 mm. thick, and was about 0.4 mm. wide.

Several photographs were taken, and figs. 5, 6, and 7 show some of them. In the case of fig. 5 there was atmospheric pressure in the box and no magnetic field. The photograph shows the scattering of the β -rays in air, and why it was necessary to work with the air at very low pressure. In fig. 6, the box was evacuated and there was no field, the exposure lasting 20 hours. In fig. 7, the box was also evacuated, but there was a magnetic field of 256 Gauss. There were several photographs taken in this way, all with similar results. In one of them the β -rays had first to pass through 0.12 mm. of aluminium.

The exposure for fig. 7 was 36 hours. The narrow band in this figure is mainly due to phosphorescence at the active material, and serves as a central band to determine the ranges of velocity of the β -rays. The other band, or magnetic spectrum, on comparison with the band in fig. 6, shows at once that the β -rays from the active material are by no means homogeneous, but that their velocities cover a wide range. It can be seen in this band that the intensity fades away on each side of the maximum, the limits being difficult to fix with certainty.

Knowing $AS = 1.49 \text{ cm.}$, $SP = 1.61 \text{ cm.}$, we can calculate the radius of curvature R of the path of the β -rays in a magnetic field H . If d be the deflection measured on the film,

$$R = \frac{SP(AS + SP)}{2d} \text{ approx.}$$

Then, if e/m be the ratio of charge to mass of β -rays of speed v , e/m_0

the same ratio for very slow speeds, c the velocity of light, we can calculate the velocities of the rays from the equations

$$\frac{mv}{e} = HR,$$

$$\frac{e}{m} = \frac{e}{m_0} \sqrt{1 - \frac{v^2}{c^2}} \text{ (Lorentz's equation),}$$

e/m_0 being taken $= 1.74 \times 10^7$ E.M.U.

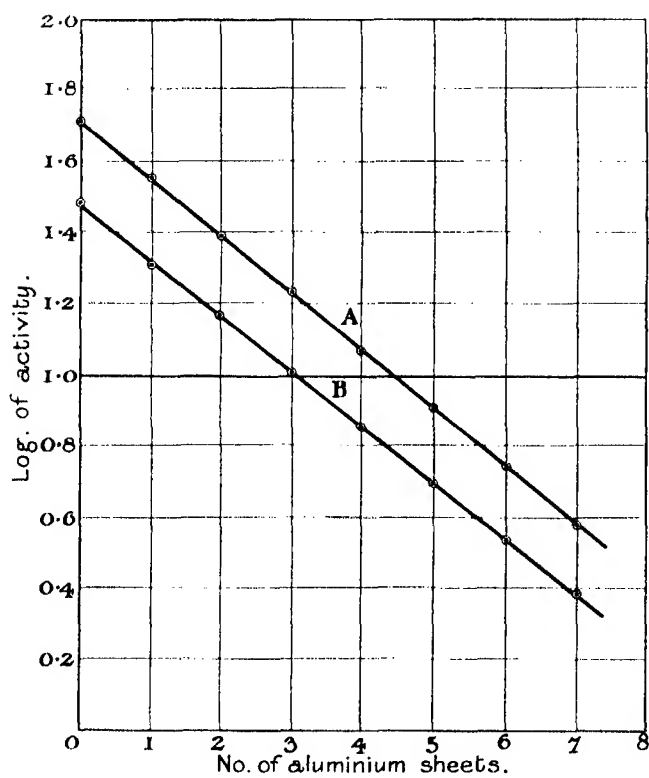
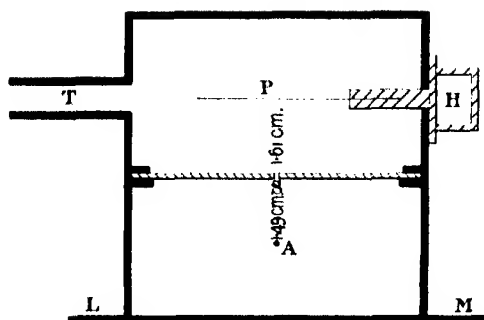
In this way it was found that mv/e for the rays had all values between 3750 Gauss cm. and 1000 Gauss cm., or v between 2.70×10^{10} cm. per second and 1.47×10^{10} cm. per second.

It is scarcely possible to fix with certainty the velocity for which there is the maximum number of β -particles. An approximate determination has been made by measuring the distance between centre of narrow band and position of maximum intensity on the film magnetic spectrum and then calculating HR . The value found for HR was 2300 Gauss cm., giving a velocity of 2.4×10^{10} cm. per second. This result agrees fairly well with that of Schmidt,* who found $HR = 2178$ Gauss cm. by the electrical method.

From the above, we see that β -rays, which are very nearly absorbed according to an exponential law, are by no means homogeneous. Now, if we have a mixture of β -rays of different speeds and take an absorption curve, the slower rays will be cut down more in proportion than the faster rays, so that the absorption coefficient should decrease as the rays traverse matter, provided there is no change in velocity. If the absorption coefficient is to remain the same or increase, there must be a loss in velocity of β -rays in traversing matter.

The above experiments do not prove directly that the β -rays from RaE are not initially expelled at an identical speed, for it is possible that the β -rays coming from the lower layers of the active material may be so changed in velocity that an exponential law of absorption results from the mixture. However, in this case we could not expect that the rays from a thin film of RaE would be absorbed exponentially, and also we should expect a different coefficient of absorption for the thin layer. An absorption curve was taken of the β -rays from a thin film of the material used in taking the photographs. In this film the absorption of the rays in the active material is very small, and care was taken that very little secondary β -radiation entered the electro-scope, yet the rays from the RaE are absorbed exponentially. The result is shown in curve B, fig. 4, the absorption coefficient being 42 cm.^{-1} . It is therefore practically certain that the β -rays from RaE are initially expelled,

* H. W. Schmidt, 'Phys. Zeit.', 1909, p. 372.



not at an identical speed, but with widely different velocities. The experiments with radium emanation gave similar evidence with respect to the β -rays from RaB and RaC.

Summing up the experiments which, as we have seen, confirm Wilson's results, we may say that—

1. β -rays, which are absorbed according to an exponential law, are not homogeneous.

2. β -rays must fall in velocity in traversing matter, for, if not, the absorption coefficient of any mixture of rays would decrease as the rays passed through matter.

In conclusion, I wish to express my thanks to Prof. Rutherford for suggesting these experiments and for his advice and help during their progress, and also to Dr. Boltwood, who separated and purified the sample of radium D employed in these experiments.

The Decrease of Velocity of the β -Particles on Passing through Matter.

By WILLIAM WILSON, M.Sc., Hon. Research Fellow of the University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received May 6,—Read June 9, 1910.)

Introduction.

In a previous paper* it was shown that the absorption of homogeneous β -rays by matter when determined by the ionisation method does not take place according to an exponential law, as had previously been assumed, but according to a law which is practically linear.

This means that the absorption coefficient† of the rays becomes greater the further the rays penetrate the absorbing medium, and since the absorption coefficient increases with decreasing velocity of the β -rays it suggests that the rays are slowed down on passing through matter.

Some experiments were described‡ which fully confirm this view.

* Wilson, 'Roy. Soc. Proc.,' A, vol. 82, 1909.

† If β rays of intensity I fall on a layer of matter of thickness dx , the intensity is decreased by $\lambda I dx$, and λ is called the absorption coefficient of the rays. For an exponential law of absorption λ is constant.

‡ *Loc. cit.*, p. 625.

The following experiments were made in order to determine the manner in which the velocity of the rays decreases as they pass through matter and to test if the actual decrease observed is sufficient to account for the linear law of absorption.

Experimental Arrangement.

The general idea of the experiment was to separate out a beam of approximately homogeneous rays by means of a magnetic field, and to determine the velocity of these rays after passing through various sheets of matter by means of a second field.

The arrangement of apparatus is shown in fig. 1. A quantity of radium emanation corresponding to about 30 milligrammes radium bromide was used

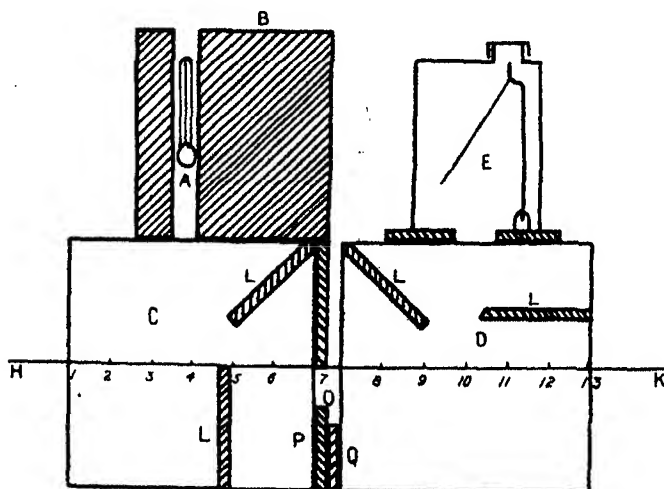


FIG. 1.

as a source of β -rays and was contained in a thin glass bulb A. This was placed in a hole 0.5 cm. diameter in a lead block B in such a manner that the rays from the active deposit could pass into the magnetic field C. The β -particles moved through the field in circular paths and passed through a hole O in a lead plate P into a second magnetic field D, where they were further deflected and made to enter an electroscope E. The mean radius of curvature in both fields was 3.5 cm. The screens L, L, L, L, were inserted in order to prevent complications due to secondary and scattered rays.

The pole-pieces of the two magnets were separated by two lead plates, P and Q. In P the hole O was cut, while in Q there was a slot in which various sheets of aluminium could be inserted to cover the hole O. The whole was securely clamped in order to prevent movements of the apparatus when the current in either electromagnet was switched on or off.

The first point to decide in connection with the apparatus is the constancy of the fields between the pole-pieces of the two electromagnets. For this purpose, readings were taken of the field strength at different points, such as those shown in fig. 1, by 1, 2, 3, . . . 13, along the line HK. The points were 1 cm. apart. The results obtained are shown in fig. 2, the positions in the field being taken as abscissæ and the strengths of the field as ordinates. We see that there is a sudden change in the field as we pass from between the pole-pieces of one magnet to between those of the other, and that the fields in each are practically uniform.

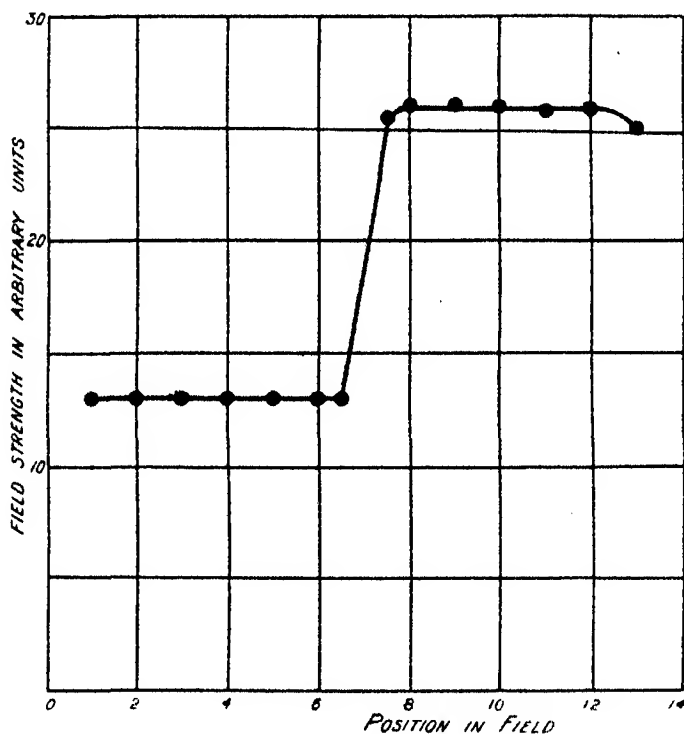


FIG. 2.

The field in each electromagnet is a function of the current in both. Thus, if the current through the electromagnet C was kept constant and that in D made to vary, changes took place in both the fields C and D. Now, in the present case, it is required that the field in the electromagnet C should be kept constant, while that in D is made to vary, so that changes in the currents exciting both electromagnets are necessary. The system was therefore calibrated as follows:—The current in the electromagnet C was kept constant, while that in D was varied, and the strengths of the fields in each were

determined by means of a Grassot fluxmeter, for each value of the current in D. A similar set of readings was taken for about ten different values of the current in C. From the results thus obtained, curves could be drawn from which the values of the currents in C and D could be adjusted so that the field in C was kept constant while that in D was made to vary.

Method of Experiment.

The method of conducting an experiment was as follows:—By passing currents of known strength through the electromagnets C and D, approximately homogeneous radiation was allowed to pass through the hole O into the magnetic field D. The field in D was varied, while that in C was kept constant, so that the same bundle of approximately homogeneous rays passed through the hole O during the whole of an experiment. The ionisation in the electroscope was determined for each value of the field in D, and the values thus obtained were plotted against the current through D. The rays were then made to pass through various sheets of aluminium placed in the slot in Q before they entered the second magnetic field, and the experiments repeated. Curves obtained in this manner are shown in fig. 3, and have well defined maxima. If the source of the rays and the

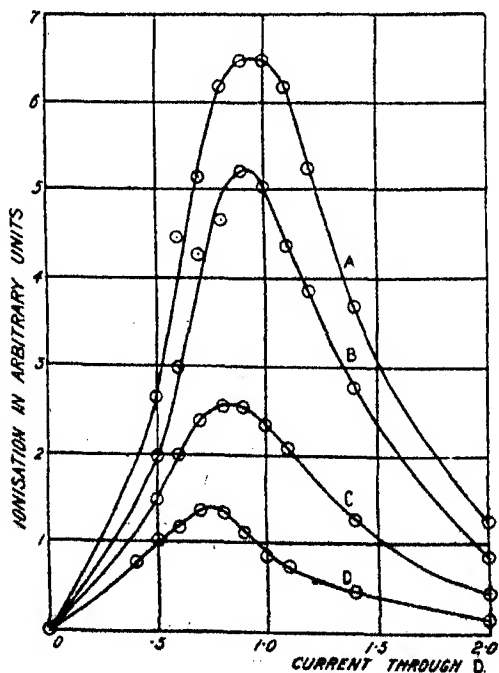


FIG. 3.

apertures between the fields and under the electroscope were infinitely small, the rays entering the second field would be quite homogeneous, and we would only get ionisation in the electroscope for one definite value of the field in D. . Since the conditions of the experiment require that these should have some finite size we get instead a curve which rapidly rises to a maximum, which may be taken as a measure of the mean velocity of the rays. It will be noticed that these maximum points move to the lower fields as sheets of aluminium are interposed in the path, proving conclusively that the velocity of the rays decreases by an appreciable amount as they pass through matter. The effects observed cannot be due to heterogeneity of the rays which pass into the second field, for if this were the case, and there were no change in the velocity of the rays on passing through matter, the maximum point would move to the higher instead of the lower fields, owing to the fact that the slow rays are more easily absorbed than the rapid ones.

Schmidt* looked for this effect with the rays from radium E, which were supposed to be homogeneous. He found no change in the position of the maximum when various sheets of metal were interposed in the path of the rays before they entered the magnetic field. These rays are, according to the view put forward in my previous paper, heterogeneous, and this accounts for the fact that the maximum point does not show any appreciable change of position. The greater absorption of the slow than of the rapid rays tends to move the maximum point to the higher fields, while the decrease in velocity tends to move it in the opposite direction. The two effects are of the same order of magnitude, and no appreciable movement of the maximum point takes place.

Returning to the present experiments, if screens were placed under the electroscope instead of between the two magnetic fields, the maximum point was found to move slightly to the higher fields, on account of the rays being not quite homogeneous. This effect was not so strongly marked for the rapid as for the slow rays.

The field-strengths corresponding to the various maxima could be determined from the calibration curves, and the velocities deduced. By this means, the manner in which the velocity of the β -rays falls off with thickness of matter traversed can be determined.

When the β -particles fall on matter, a certain proportion are sent back, a certain proportion absorbed, and those which pass on do so with diminished speed. Thus, in the present experiments, we have, besides a movement of the maximum to the lower fields, a considerable decrease in the number of

* Schmidt, 'Phys. Zeit.', 8, 1907, p. 361.

particles reaching the electroscope when sheets of matter are inserted in the path of the rays. This makes it impossible to continue measurements after the β -particles have passed through a small thickness of aluminium. Experiments were therefore carried out as follows:—Particles moving at a high speed were started with, and their velocity determined after they had passed through various thicknesses of matter. Another experiment was then started, with the initial velocity intermediate between the first and last of the former set of readings, and similar measurements made. This process was repeated until rays of such low velocity were reached, that their rate of absorption became altogether too great to admit of any accurate determination of the maxima.

Discussion of Results.

Results obtained in this manner are shown in Table I. The portions into which the table is divided refer to experiments starting with different initial points.

Table I.

Thickness of aluminium in mm.	H ρ in Gauss cm.		Velocity in 10^{10} cm./sec.		Energy in 10^{-7} ergs.	
	Screen under electroscope.	Screen between fields.	Screen under electroscope.	Screen between fields.	Screen under electroscope.	Screen between fields.
0.245	5280	4980	2.85	2.83	17.6	16.2
0.489	5280	4500	2.85	2.80	17.6	14.3
0.067	4750	4250	2.819	2.78	15.2	13.6
0.245	4780	4100	2.818	2.77	15.2	12.9
0.489	4800	3620	2.820	2.71	15.2	10.6
0.731	4730	3180	2.818	2.68	15.2	8.7
0.067	3770	3690	2.78	2.72	11.4	11.1
0.245	3800	3420	2.735	2.68	11.4	10.0
0.489	3800	3000	2.735	2.60	11.4	8.1
0.067	2520	2250	2.475	2.38	6.2	5.2
0.245	2850	1950	2.565	2.25	7.5	4.1

The velocities are calculated from the formula $mv/e = H\rho$ where H is the strength of the field and ρ the radius of the path of the rays. The value of e/m was determined from the Lorentz-Einstein formula

$$\frac{e}{m} = \frac{e}{m_0} \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}},$$

where c is the velocity of light. The value of e/m_0 is taken as 1.74×10^7 E.M.U.*

* Bucherer, 'Phys. Zeits.', 9, 1908, p. 755.

The corresponding values of the energy are calculated from the equation given by Einstein.*

$$E = m_0 c^2 \left\{ \left(1 - \frac{v^2}{c^2} \right)^{-\frac{1}{2}} - 1 \right\}.$$

Now, according to the experiments described in my previous paper, the absorption of the β -rays takes place according to a linear law when measured by the ionisation. That is, the rays after passing through a given thickness of matter x have an intensity given by

$$I = k(a - x),$$

where k and a are constants.

The absorption coefficient is defined by λ where $\lambda I dx = -dI$, or

$$\lambda = -\frac{1}{I} \frac{dI}{dx} = \frac{1}{a - x}. \quad (1)$$

Thus the value of λ increases as the thickness of matter increases from zero, becoming theoretically infinite when $x = a$.

In the previous paper a table was given showing the connection between λ and the velocity of the β -rays, and from it we can find the velocity of rays with any given absorption coefficient.

Now from equation (1) we can determine the absorption coefficient of rays of any initial velocity after they have passed through any given thickness of matter, and hence can deduce the corresponding velocity. Results obtained in this manner are shown in Table II, where the initial velocity of the rays is 2.86×10^{10} cm./sec.

Table II.

Thickness of Al in mm.	λ in cm. ⁻¹ .	Velocity in 10^{10} cm./sec.	Energy in 10^{-7} ergs.
0.00	4.7	2.86	18.6
0.51	6.2	2.80	14.3
0.83	7.7	2.75	12.0
1.03	9.1	2.70	10.4
1.20	10.8	2.65	9.2
1.34	12.7	2.60	8.1
1.48	15.4	2.55	7.15
1.58	18.2	2.50	6.5
1.66	21.3	2.45	5.9
1.72	24.1	2.40	5.4
1.78	28.6	2.35	4.9
1.82	32.3	2.30	4.5
1.86	37.0	2.25	4.1
1.88	40.0	2.20	3.8
1.95	55.5	2.00	2.75

* Einstein, 'Ann. der Physik,' June, 1907.

The results obtained in this manner were compared with those determined experimentally as follows:—Starting with rays of a certain observed velocity, we can calculate what their velocity should be after passing through various thicknesses of matter, and these results can be compared with those actually determined. Such starting points are shown in Table III in square brackets. The values of the velocities after the rays have passed through various sheets of aluminium are shown in Column 4, and the corresponding velocities calculated as above in Column 5. The various sections of the table refer to experiments with different starting points. The agreement is seen to be good, except in the case of some of the low velocities, which are difficult to determine.

Table III.

Thickness of matter in mm.	H ρ in Gauss cm.		Velocity in 10^{10} cm./sec.	
	Observed.	Calculated.	Observed.	Calculated.
0	5280	5420	2.85	2.80
0.245	[4980]	[4980]	[2.83]	[2.83]
0.489	4500	4520	2.80	2.80
0	4800	4850	2.82	2.825
0.245	[4390]	[4390]	[2.79]	[2.79]
0.489	3850	3950	2.74	2.75
0.731	3340	3510	2.67	2.69
0	4630	4560	2.82	2.81
0.067	4250	4430	2.78	2.79
0.245	[4100]	[4100]	[2.77]	[2.77]
0.489	3620	3690	2.71	2.715
0.731	3130	3290	2.63	2.65
0	3770	3850	2.735	2.74
0.067	3690	3740	2.72	2.725
0.245	[3420]	[3420]	[2.68]	[2.68]
0.489	3000	3000	2.60	2.60
0.245	2750	2720	2.54	2.535
0.489	2370	2600	2.425	2.50
0.067	2250	2390	2.385	2.42
0.245	1950	2400	2.25	2.42

In the last two sections of the table the starting points are not shown, since they were different for each different thickness of matter. The position of the maximum point moved appreciably to the higher fields when sheets of different thickness were placed under the electro-scope, and these positions were taken as starting points.

The experiments become very difficult when rays of low velocity are being dealt with, owing to the fact that they are both very easily scattered and very easily absorbed by the screens which are placed in their path.

The decrease of velocity with thickness of matter traversed is shown graphically in fig. 4. The curve is drawn from the results given in Table II, and the points denoted by circles are the experimental values given in

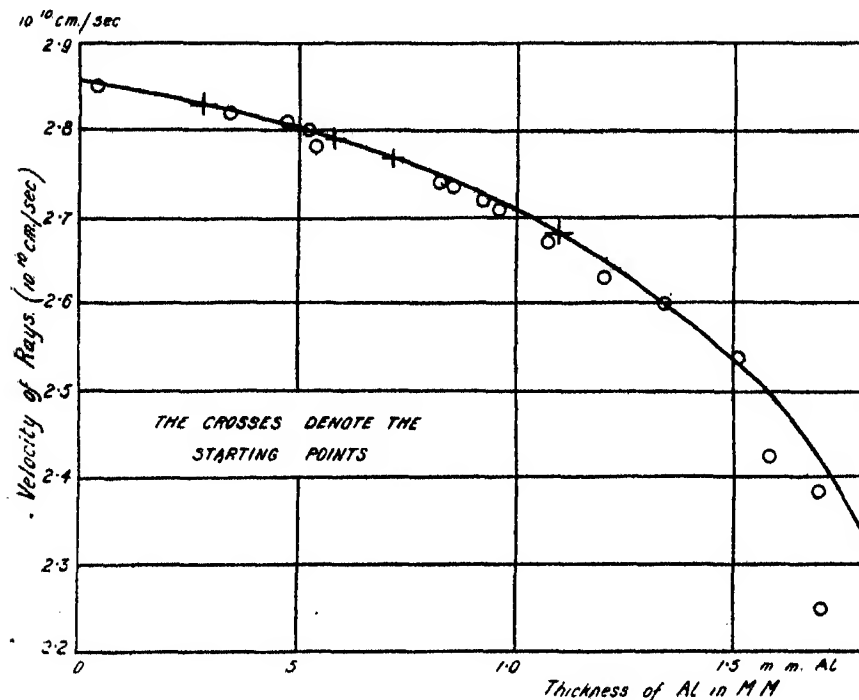


FIG. 4.

Table III. The values in square brackets are fitted on the curve, and the remaining points are determined from these starting points.

Now although the total change of velocity observed in these experiments is small it is quite definite, and since we are dealing with rays of high velocity the change in the energy and in the properties of the rays with respect to absorption are quite great. Taking the difference between the highest and lowest values of the velocity observed, the change is only from 2.85 to 2.25×10^{10} cm./sec., *i.e.*, only 21 per cent. The change of energy corresponding to this is from 17.6 to 4.1×10^{-7} ergs, or a difference of 77 per cent. The change in the value of the absorption coefficient is still more marked, for that corresponding to the higher velocity is 4.8 cm. $^{-1}$ while that corresponding to the lower is 35.7 cm. $^{-1}$, which shows that the penetrating power of the rays has been completely altered.

The Law of Decrease of the Velocity of the β -rays as they penetrate Matter.

By considerations of the energy given up by the β -particles to the matter with which they come into contact Sir J. J. Thomson* has deduced that the energy of the rays as they penetrate matter should fall off according to the law $E^2 = k(a - x)$ where E is the energy of the rays, x the thickness of matter traversed, and k and a constants. The results for the range of velocities examined are in better agreement with the formula $E = k'(a' - x)$, but it is hard to distinguish between the two, as the determinations of the low velocities are uncertain. The indirect results given in Table II agree very well with this latter equation except at the end, where the decrease of E with regard to x becomes more rapid.

Conclusion.

The experiments show that the velocity of the β -particles is appreciably reduced as they pass through matter and that the magnitude of the change is such as would be expected from the linear law of absorption.

I wish to thank Professor Rutherford for his many valuable suggestions and for his kind interest in this work.

* 'Conduction of Electricity through Gases,' 2nd edit., p. 378.

Rate of Emission of α -Particles from Uranium and its Products.

By J. N. BROWN, A.R.C.S.

(Communicated by Prof. the Hon. R. J. Strutt, F.R.S. Received May 24,—
Read June 9, 1910.)

The object of this investigation was to find directly how many α -particles are emitted per second per gramme of uranium in equilibrium with all its products. The number can be calculated from the rate of emission of the particles from radium, determined by Rutherford, but no direct experiment has previously been performed with uranium as it occurs in Nature.

To estimate the number of α -particles emitted, their well-known property of producing scintillations when they strike a zinc sulphide screen (each α -particle producing one scintillation) was employed. The scintillations were observed through a microscope provided with a special objective.

The uranium ore employed was pitchblende. This, owing to its large density and the consequent small distance of penetration of α -particles into it, had to be prepared in very thin layers in order that all the pitchblende used might be effective. The films of pitchblende used were made as follows:—

The mineral was first converted into a fine powder by grinding it up with chloroform in an agate mortar. A small quantity of the powdered pitchblende was then suspended in chloroform in a dish, at the bottom of which was placed a light copper disc of known weight. As the chloroform evaporated the pitchblende was deposited on the copper disc in a film of suitable thickness.

The copper disc with the film of pitchblende on it was first weighed and then placed on the stage of a microscope. Over the film was placed a zinc sulphide screen, supported on a small wire tripod, so as to be as near as possible to the pitchblende without actually touching it. The screen would consequently receive all the α -particles emitted by the pitchblende beneath it over a range of 180° , and hence the number observed could be doubled in order to obtain the full emission. The microscope was fitted with a wide-angle objective in order to make the scintillations produced by the α -particles as bright as possible.

The scintillations had to be counted in a dark room, but it was found best to illuminate the field slightly, as recommended by Regener,* so as to make

* 'Verh. d. D. Phys. Ges.,' vol. 10, p. 78, 1908.

sure that the eye did not shift from over the top of the microscope. The required illumination was obtained by connecting a 110-volt lamp to 50-volt terminals, a piece of black paper being fitted over the top of the microscope to shut off stray light.

The time required for 100 scintillations* to be produced in the field was now measured by means of a stop-watch, readings being taken for various parts of the film and a mean obtained. Each scintillation was caused by the impact of one α -particle against the screen.

Measurements were made with films of different thicknesses, and a curve finally plotted between weight of film and number of scintillations per minute. In accordance with the known properties of the α -rays, if the α -particles had all come out normally to the surface, this curve should have been a straight line through the origin up to a certain point, beyond which the line should have been horizontal. The curve actually obtained did not change its direction quite so suddenly, the more gradual change being doubtless due to the fact that the portion of the film immediately beneath the objective was surrounded by more pitchblende from which α -particles, emitted obliquely, could reach the screen. The result had, of course, to be calculated from a film for which the curve showed the rate of production of scintillations to be proportional to the thickness.

The diameter of the film and also that of the field of the microscope were afterwards measured, the latter being obtained by traversing across the field a small strip of metal on which a fine line was ruled. This strip was attached to a travelling microscope, and the readings of the latter taken when the line first appeared in the field and when it left it.

The percentage of uranium in the pitchblende had now to be estimated. The method employed for the analysis depended upon precipitating the uranium as phosphate, $(\text{UO}_2)_2\text{P}_2\text{O}_7$, in which the percentage of uranium by weight is 68.55. About 0.5 gramme of the finely powdered pitchblende was submitted to various processes in order to separate the uranium from silica and other substances present. To the solution remaining after these substances had been eliminated was added about 3 grammes of microcosmic salt, the solution being made just alkaline with ammonium hydrate. A few drops of dilute nitric acid and a solution of 10 grammes $\text{Na}_2\text{S}_2\text{O}_3$ in water were added, and the whole boiled for half an hour. The yellow precipitate was collected, washed with hot water, dried in the steam oven, detached from the paper and ignited over the blow-pipe till of constant weight. The

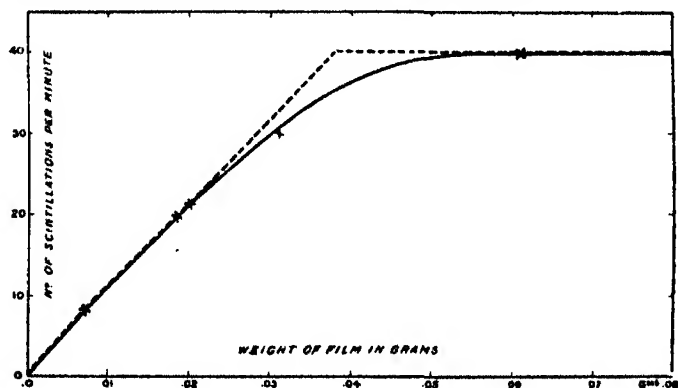
* It has been found by Rutherford that the error due to the irregular rate at which the scintillations are produced cannot be eliminated by observing less than 100. See 'Roy. Soc. Proc.,' A, vol. 81, p. 159.

filter paper was incinerated, and the ash added to the contents of the crucible. The green mass was completely soluble in strong nitric acid, and therefore consisted entirely of $(\text{UO}_2)_2\text{P}_2\text{O}_7$.

This completed the data from which to calculate the rate of emission of α -particles from uranium. The results were as follows :—

Weight of film.	Diameter.	Time for 100 scintillations.	Number per minute.
grammes.		seconds.	
0·0069	3·77	740	8·1
0·0184	3·77	302	19·9
0·0201	3·77	283	21·2
0·0310	3·75	200	30·0
0·0611	3·77	150	40·0

The curve obtained from these results is as follows :—



The diameter of the field of the microscope was 0·126 cm.

The result of the analysis of the pitchblende was—

Weight of pitchblende used.	Weight of precipitate obtained. (UO_2) ₂ P ₂ O ₇ .	Percentage of uranium in pitchblende.
grammes.	grammes.	
0·5155	0·3137	$\frac{0·3137 \times 0·6855}{0·5155} = 41·73$
0·5240	0·3201	$\frac{0·3201 \times 0·6855}{0·5240} = 41·87$
Average percentage of uranium = 41·80		

Now, considering the film weighing 0·0201 gramme, for which the number of scintillations was 21·2 per minute,

Weight of uranium contained in the film = $0·0201 \times 0·418$.

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Hence

Number of scintillations per sec. per gramme of uranium over 180°

$$= \frac{21 \cdot 2 \times (3 \cdot 77)^2}{60 \times 0 \cdot 0201 \times 0 \cdot 418 \times (0 \cdot 126)^2}$$

Doubling this to obtain the total emission over 360° , we have—

Number of α -particles emitted per sec. per gramme of uranium

$$= \frac{2 \times 21 \cdot 2 \times (3 \cdot 77)^2}{60 \times 0 \cdot 0201 \times 0 \cdot 418 \times (0 \cdot 126)^2} = 7 \cdot 86 \times 10^4.$$

Rutherford* finds that 1 gramme of radium in equilibrium with radium emanation and A, B, C, gives $13 \cdot 6 \times 10^{10}$ α -particles per second.

This includes four α -ray changes. There are, in addition, two changes in uranium, one in ionium and one in polonium, making four more, and an effect due to actinium, probably very small. Neglecting this last, the other bodies will bring up the total to $27 \cdot 2 \times 10^{10}$ per second per gramme of radium, or $27 \cdot 2 \times 10^{10} \times 3 \cdot 4 \times 10^{-7}$ per second per gramme of uranium; *i.e.* $9 \cdot 25 \times 10^4$, which is in fair agreement with the above result.

I am indebted to Prof. Strutt for suggesting the research, and for much valuable advice during its progress; my thanks are also due to Mr. C. S. Garland, A.R.C.S., B.Sc., for kindly estimating the percentage of uranium in the pitchblende.

* 'Roy. Soc. Proc.' A, vol. 81, p. 156.

On Radiation in a Gaseous Explosion.

By BERTRAM HOPKINSON, F.R.S.

(Received May 24,—Read June 9, 1910.)

In the first report of the British Association Committee on Gaseous Explosions, attention was drawn to the probable importance of radiation in determining the rate of cooling of the mass of hot gas produced by igniting an inflammable mixture in a closed vessel. In the second report reference was made to some experiments which I had made on the effect of coating the walls of the explosion vessel with bright tin-foil. It was found that if a mixture of coal-gas and air of given composition were exploded in a vessel thus lined, the maximum pressure reached was nearly the same as that given by an identical mixture when the tin-foil lining was blackened, but the rate of cooling was decidedly less.

Though the experiment established a substantial difference between the rates of heat-loss in the two cases, it was hardly sufficient to justify giving quantitative results, nor was it absolutely conclusive as to the cause of the difference, though it seemed highly probable that it was due to the difference in the power of the walls to absorb radiant energy.

I have recently completed a more elaborate series of tests, which I think are sufficiently accurate and conclusive for publication. Instead of coating the inside of the vessel with tin-foil, I have had it plated with silver, which has in successive explosions of the same mixture been first highly polished and then blackened. As in the vessel lined with tin-foil, the cooling is slower when the walls are reflecting, but the difference is greater with the silver-lined vessel, amounting to about 50 per cent. during the first quarter of a second. Moreover, there is a difference in maximum pressure, amounting to about 3 per cent. Records have also been obtained of the change of temperature, during the explosion and subsequent cooling, of a bolometer placed outside a window of fluorite in the wall of the vessel, and these have shown that for one-tenth of a second after maximum pressure something like one-third of the whole heat-loss to black walls is due to radiation, and that the radiation is still perceptible half a second after maximum pressure, when the temperature of the gas has fallen to about 1200° C. Of the whole of the heat given up by the gas in cooling from 2100° C. to atmospheric temperature at least one-fifth part goes in radiation.

The explosion vessel employed was cylindrical, the internal dimensions being 30 cm. by 30 cm. It was made of cast iron, and the inner surface

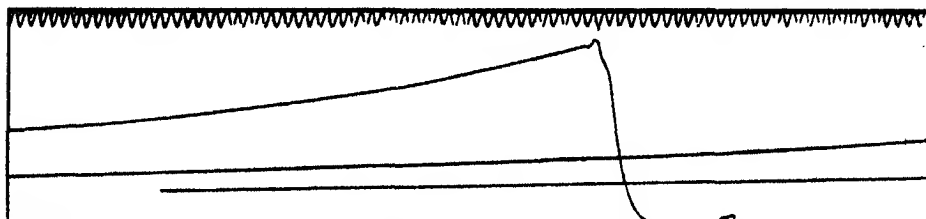
after finishing in the lathe was electro-plated. The polishing was done at first by hand with a leather and rouge, but though this gave a surface which to all appearances was perfectly polished, it was found that appreciably higher pressures and much slower cooling could be obtained by putting more work into the polishing. Accordingly in the later trials a motor-driven buffing wheel was used, and the surface was also carefully washed with alcohol. For blackening the surface, a dead black paint consisting of lamp-black mixed with a little shellac was put on in a thin layer. The weight of this layer when dry was about 1.5 milligramme per square centimetre, and the thickness about 0.02 mm.

The explosive mixture consisted always of 15 parts of Cambridge coal-gas, having a higher calorific value (as determined with a Boys' calorimeter) of about 370 lb.-centigrade thermal units per cubic foot, or say 6000 calories per litre under standard conditions, to 85 of air; this being very nearly the mixture of maximum strength consistent with complete combustion. The mixture was at atmospheric pressure and temperature before firing. The products of combustion contained (by volume) about 8.5 per cent. of CO_2 , and 20 per cent. of H_2O , the remainder being nitrogen with a small amount of excess O. In order to secure strictly comparative results a mixture of gas and air containing about 19 per cent. coal gas was stored in a separate tank for from 3 to 12 hours. A portion of this mixture was then transferred to the partially exhausted explosion vessel, being there diluted with sufficient air to give the required strength of 15 per cent. There was sufficient mixture in the tank to give three or four explosions, and, the quantity of air left in the explosion vessel before admitting the mixture from the tank being only about one-fifth of the whole, small errors in the measurement of this quantity were without appreciable effect upon the strength of mixture, which must have been substantially identical for all charges taken from the same filling of the tank. The first explosion was taken with the vessel highly polished. It was quickly followed with a second explosion of the same mixture, the walls having been in the meantime either repolished or blackened, and a third and sometimes a fourth explosion with blackened walls was taken. In this way three or four explosions were made, one or more of which were with polished walls and the remainder with blackened walls. The conditions for these explosions were identical not only as regards the composition of the charge but also in respect of barometric pressure and temperature.

The pressures were recorded in about 20 cases by a pencil indicator of the outside-spring type made by Dreyer and Company, the ordinary reciprocating drum of which was replaced by a revolving drum driven

through worm gearing by an electric motor. In order to reduce friction, smoked paper and a fine point on the indicator were used instead of the usual pencil. A facsimile of a diagram so obtained is shown in fig. 1, from

FIG. 1.—Record No. 19.



0.76 of original size. Scale of reproduction, 1 cm. = 4.7 lbs. per sq. in.

which it will be seen that there is slight oscillation due to the inertia. In the results recorded below a correction has been applied for these oscillations, a smooth curve being drawn in each case, but the maximum pressure is uncertain, perhaps by as much as 1 lb. per square inch. Six diagrams were also taken with the optical indicator of the piston and spring type which I designed some years ago for gas-engine work. Two diagrams given by this indicator are reproduced in fig. 2.* This diagram shows no

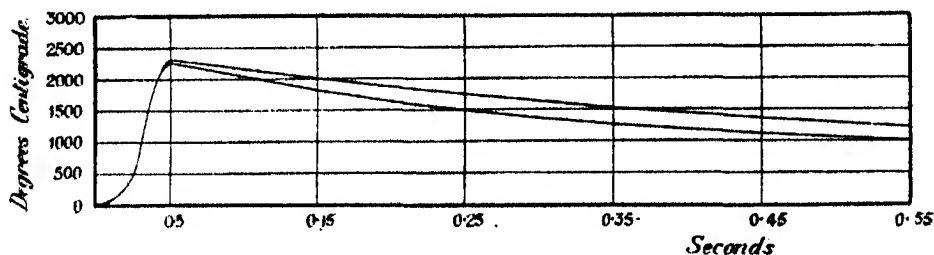


FIG. 2.

oscillation, and is probably in every respect more accurate than that given by the pencil instrument. It may be observed, however, that the errors of the latter instrument would not affect comparisons of different explosions taken under the same circumstances, except perhaps as regards maximum pressure.

In order to show the degree of accuracy reached it has been thought desirable to give all the results of the 27 satisfactory records which were obtained. Particulars of the procedure adopted in polishing are also given

* These diagrams, as also figs. 4 and 7, are exact tracings from photographic enlargements of the originals, the tracing being subsequently reduced in reproduction for printing.

Table I.

		Pressure, lbs. per square inch.				Polishing.
Record No.	Maximum pressure.	Times after ignition, secs.				
		0.15	0.25	0.35	0.45	
Pencil Indicator.						
1	111.9	96.6	86.2	76.5	—	First record taken in this vessel; polished with dry rouge.
2	109.0	95.0	82.7	74.2	—	Hand-polished with wash-leather.
3	107.8	85.5	68.3	58.0	50.5	Blackened.
4	109.0	—	72.5	—	—	Hand-polishing after blackening for (3).
5	107.6	—	72.4	—	—	Hand-polished.
6	105.9	83.3	68.2	57.5	49.9	Blackened.
7	109.5	97.0	84.2	—	—	Polished with motor-driven buff and dry rouge.
8	110.5	93.8	80.1	68.5	—	Hand-polished with wash-leather.
9	110.0	84.2	67.5	56.4	49.4	Blackened.
10	110.0	93.1	79.4	69.0	—	Polished with motor-driven buff and dry rouge.
11	110.0	92.6	79.0	69.5	—	Hand-polished.
12	111.7	87.0	71.9	61.0	53.5	Blackened.
13	110.4	87.0	70.8	60.1	52.5	"
14	111.0	98.6	88.4	79.6	71.0	Polished with motor-driven buff and rouge mixed with methylated spirits, re-washed with methylated spirits and hand-polished.
15	110.0	93.3	81.2	70.0	—	Hand-polished.
16	110.6	87.3	70.8	60.4	52.3	Blackened.
17	108.1	86.2	70.4	59.4	51.3	"
18	112.9	98.4	86.3	76.3	67.2	Polished as in (14).
19	112.0	95.1	81.1	—	—	Ditto, re-washing with methylated spirits omitted.
20	111.4	98.4	86.2	75.5	67.2	Polished as in (14).
21	110.2	86.3	71.1	60.3	53.0	Blackened.
Optical Indicator.						
I	114.0	98.7	84.2	73.5	64.9	Highly polished motor-driven buff and rouge, washed with methylated spirits and again polished.
II	114.0	98.7	84.2	73.5	65.4	Ditto.
III	110.8	89.2	73.1	61.3	53.5	Blackened.
IV	114.9	99.0	85.4	73.5	64.9	Highly polished as in I and II.
V	111.6	89.5	73.9	62.1	53.8	Blackened.
VI	111.2	89.1	73.9	62.1	54.7	"

in each case, as it was found that this had a material effect upon the results. The trials are separated into groups, each group being taken from one lot

of mixture in the tank, as described above. The barometric pressure and temperature varied from one group to another, and in order to make the results comparable the pressures recorded have all been reduced to a standard barometer of 760 mm. and a standard temperature of 12° C., on the assumption that the absolute pressure is proportional to the barometric height and inversely proportional to the absolute temperature of the mixture before explosion. In comparing the results of one day with another day it should, however, be remembered that the calorific value and composition of the gas vary slightly from day to day.

Looking first at the records of the explosions in which the walls were blackened, it will be seen that the two cooling curves from the same mixture agree at all points within 1 lb. per square inch. With the optical indicator (V and VI) the agreement is closer, and here it extends also to the maximum pressure. On account of oscillation the pencil indicator is not so reliable at maximum pressure. The results may be summarised as follows :—

Table II.—Blackened Walls.

	Maximum pressure.			0.25 sec.		
	Min.	Max.	Mean.	Min.	Max.	Mean.
Pencil (8 cards)	105.9	111.7	109.3	68.2	71.9	70.0
Optical (8 cards)	110.8	111.6	111.2	73.1	73.9	73.6

The optical indicator reads appreciably higher than the pencil instrument. This may be partly due to a change in calorific value, but it is probable that there is also some difference between the instruments. Both were calibrated with dead weights.

The "polished" records do not show such good agreement, and it is at once apparent that the procedure followed in polishing is important, differences hardly apparent to the eye greatly affecting the rate of cooling. The 13 pencil records with polished walls show at 0.25 second pressures ranging from 72.4 to 88.4 lbs. per square inch, a range of 16 lbs. Explosions of identical mixtures give cooling curves which differ at this period by 5 or 6 lbs. per square inch. This uncertainty disappeared largely but not entirely after record 14, when the practice was adopted of washing the surface with methylated spirits so as to remove all traces of the shellac used in the previous blackening. By combining this washing with the use of a motor-driven buff more consistent results were obtained.

In what follows reference will only be made to those "polished" records in which this procedure was followed, namely, Nos. 14, 18, 20, 21, I, II, and IV. The results of these experiments agree moderately well, but it is evident that there are still differences in the walls which substantially affect the rate of cooling, though quite inappreciable to the eye.

(a) *Maximum Pressure*.—The maximum pressure reached with the polished walls is in every case higher than that reached with the blackened walls. The difference shown by the pencil indicator is in one group (14, 16, 17) 1.7 and in the other group (18, 20, 21) 1.9 lb. per square inch, the mean being 1.8; while the differences shown by the optical indicator are respectively 3.2 and 3.5 lbs. per square inch, the mean being 3.3. Taking the optical indicator as probably the more accurate, it follows that the maximum temperature reached with a polished lining is approximately 70° higher than that reached with the blackened lining. In considering this result it is to be remembered that the volumetric heat of the products of combustion is probably about 50 per cent. greater at this temperature than is the mean volumetric heat between 100° C. and 2000° C., so that the 3 per cent. difference in maximum temperature may represent something like 5 per cent. difference in total thermal energy. It is probable, however, that this 5 per cent. is not wholly represented by a difference in the heat which has been lost to the walls, but that it is partly due to incompleteness of combustion. At the moment of maximum pressure the rate of transformation of chemical into thermal energy just balances the rate of loss of heat to the walls. This heat loss being less when the walls are polished, the percentage of uncombined gas will also be less, since the rate of transformation of energy diminishes with the amount remaining to be transformed. Any effect of the reflecting state of the walls on the rate of combustion or on the ultimate state of equilibrium would, of course, invalidate this argument; such an effect is not impossible, but I have not yet discovered any evidence of it.*

(b) *Rate of Cooling*.—That the gas cools more slowly when the lining is reflecting is at once obvious from Table I or from fig. 2, which shows records I and III, obtained with the optical indicator from the explosion of

* Some recent experiments by Mr. W. T. David suggest that the state of equilibrium is not independent of the walls. He finds that the gas radiates more strongly at a given temperature when the walls are polished. If this be so, it must mean that the energy of the molecular vibrations is a greater proportion of the whole when the walls are polished than when they are black, and, consequently, that the energy of a gas enclosed in polished walls is greater than in black walls, though the temperatures (as inferred from the pressures) are the same. In other words, the apparent specific heat of a gas varies with the vessel in which it is contained. It cannot be said that this conclusion has yet been completely established, but it suggests some interesting possibilities.

the same mixture, superposed. The following table shows the time (from the moment of ignition) taken by the gas to cool to 1700°C . and 1200°C . respectively with different surfaces. Since the heat lost by the products of explosion in cooling to a given temperature must be very nearly the same whatever the state of the walls, the times are inversely proportional to the mean rate of cooling. This ratio is shown in each case, the rate of cooling with the black walls being taken as the unit.

Table III.

Record No.	1700° C.			1200° C.		
	Black.	Polished.	Ratio.	Black.	Polished.	Ratio.
14, 16, 17	0·178	0·320	0·56	0·297	0·567	0·52
18, 20, 21	0·177	0·289	0·61	0·302	0·473	0·64
I, II, III	0·193	0·269	0·72	0·320	0·455	0·70
IV, V, VI	0·196	0·277	0·71	0·327	0·450	0·73

It will be seen that the rate of loss of heat to the polished surface varies in different observations from rather over half to about three-quarters of the loss to black walls. The differences between one experiment and another cannot be ascribed in any large measure either to errors of observation or to the indicators. Indicator errors would affect both records equally and would not affect the ratios of times. It seems quite certain that in the optical records, which were taken together after all the others, the surface was not so good. Further there seems to be no reason to doubt that in explosion 14 the rate of cooling with the polished surface was not much more than half of that with the blackened walls. The tangents to the two cooling curves at corresponding points (that is points for which the temperatures are the same) tend to become parallel as the temperature falls. The slopes of these tangents are the ratio of the rates of heat-loss, which therefore tend to equality as the gas cools.

Comparisons similar to the above with a tin-foil lining first bright and then black showed that the ratio of rates of cooling down to 1200°C . was about 0·87. If the difference between this ratio and unity be taken as a measure of the radiation reflected it will be seen that tin-foil reflects for this purpose less than half as well as silver. It is not surprising, therefore, that no difference in maximum pressure could be detected with the tin-foil lining, using a pencil indicator.

Bolometric Measurements.

Having obtained the above results, it was decided to make bolometric determinations of the actual heat-loss to the walls and of the radiation. For this purpose a recording bolometer was devised, consisting of a silver or platinum strip whose resistance could be recorded on a revolving drum at the same time as the pressure developed by the explosion. The method used for recording the temperature of the strip was the same as that which I have described in a previous paper.* Briefly, it consists in passing through the strip a constant continuous current sufficient to produce some difference of potential at its terminals, balancing this difference by means of a source of

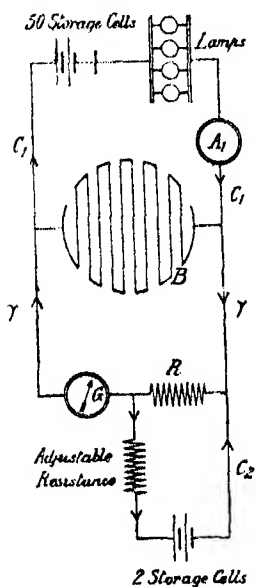


FIG. 3.

constant E.M.F., and recording by a reflecting galvanometer the increment of E.M.F. which arises when the strip is heated by the explosion. The deflection of the galvanometer is proportional to the increase in E.M.F., which again is proportional to the increase of resistance of the strip, and therefore to its rise of temperature. The connections are shown in fig. 3. The current C_1 passing through the bolometer B is taken from a number of storage cells working through a resistance high enough to ensure that the small variation of resistance in the bolometer during the explosion shall have no appreciable effect upon it. An ammeter A_1 is included in this part of the circuit, and the current is adjusted to a definite value before the experiment. The terminals of the bolometer are also connected to the recording galvanometer G through a resistance R , in which a current C_2 is maintained by means of storage cells in such a direction and of such amount that the E.M.F. at the terminals of the bolometer when cold is approximately balanced. The resistances are such that C_2 does not appreciably vary when the bolometer is warmed. When the bolometer is heated the difference of potential between its terminals rises in proportion to the rise of temperature, while the balancing difference between the terminals of resistance R remains the same except for the small change in the current flowing in it consequent on the diversion of some part of the current C_1 from the bolometer to the galvanometer circuit. This change of current in R and in the bolometer is small, but as it is recorded on the galvanometer it can be allowed for if necessary.

* 'Roy. Soc. Proc.,' A, vol. 79, p. 138.

The recording galvanometer used in these experiments was of the ballistic suspended-coil type. The coil was of the standard pattern made by Messrs. R. W. Paul, but the usual suspension, which would give a period of about 4 or 5 seconds, was replaced by a much stiffer suspension, giving a period of about $1/25$ second; and for the usual permanent magnet was substituted an electro-magnet magnetised nearly to saturation, which gave a strong and fairly constant field, whose amount could be accurately adjusted to a definite value by a comparatively rough adjustment of the magnetising current. The resistance of the galvanometer was about 3.5 ohms, and its deflection was recorded photographically on the same revolving drum as that on which the pressures were recorded by the optical indicator.

It will be obvious that with the above arrangement the deflection of the galvanometer is nearly proportional to the increase of resistance of the bolometer strip; and this is so, even though exact balance is not obtained before the explosion. In order to get the relation between these two quantities, the current C_2 was reduced to zero* when the bolometer strip was cold, and the ratio was found between the galvanometer deflection under these conditions and the current in the bolometer strip, which latter was, of course, for this purpose reduced to a fraction of the value employed when taking explosion record. If c be the current under these circumstances corresponding to any deflection of the galvanometer, then, when there is a current C_1 shown on the ammeter A_1 , the proportion of increase in the bolometer resistance corresponding to the same deflection of the galvanometer is $\frac{c}{C_1 - \gamma}$, where γ is the current in the galvanometer.

Since the rise of temperature is directly deduced from the proportion by which the resistance rises, it will be seen that the calibration of the bolometer, that is, the reduction of galvanometer deflection to temperature increase, requires only an accurate knowledge of the ratio of the currents

* Strictly speaking, this should be done by reducing the E.M.F. in the circuit C_2 to zero (short-circuiting the battery) and not by means of the adjustable resistance; and similarly the reduction of the current in circuit C_1 should be effected by a reduction in the E.M.F. of the battery. The resistances in the circuit being then all the same in calibration and in use, the relation between galvanometer deflection and change of resistance is given accurately in the manner described, being independent of the small changes in C_1 and C_2 consequent on the disturbance of the circuit by the increase of the bolometer resistance. In practice it is simpler to make the resistances in circuits C_1 and C_2 so large that they can be treated as infinite, and to use them for adjustment of current; but it must not be forgotten that any variation in either of these currents has the same effect as an equal percentage variation of the bolometer resistance. If, for example, it be desired to measure a rise of temperature of 40°C. correct to 1 per cent., the rise of resistance amounts to perhaps 15 per cent., and consequently C_1 or C_2 must be constant to within 1 part in 600.

c and C_1 , together with a rough knowledge of the galvanometer current γ , provided the latter is small compared with C_1 . In the experiments under consideration, γ never exceeded about 1 per cent. of C_1 , and could be neglected altogether.

(1) *Polished and Blackened Silver*.—The first bolometer used consisted of a plate of chemically pure silver, $1/5$ mm. thick, cut up so as to make a continuous strip having a resistance of 0.065 ohm at 14° C. The weight of the silver per square centimetre was 0.210 gramme, and it was mounted on a backing of linoleum $\frac{1}{4}$ inch thick, which was fixed on to the flat end-cover of the explosion vessel, a little above the centre. The temperature coefficient of the resistance of the silver was measured, and found to be 0.0040; its specific heat was assumed to be 0.056. The silver strip was fixed to the linoleum by means of shellac varnish and a few pins. Comparative records were taken with this bolometer first polished as highly as possible, and then blackened over, sometimes with the same blackening mixture as was used in the experiments described above, and sometimes with camphor smoke. The layer of black on the silver slightly increases its thermal capacity. The layer weighed something under 1 milligramme per square centimetre, equivalent to perhaps 0.2 milligramme of water, which is less than 2 per cent. of the heat capacity of the silver. This small addition is neglected in what follows, the heat capacity of the bolometer being supposed the same whether blackened or not. A considerable number of records were taken with the bolometer in these two states. The rest of the surface was blackened in all cases.

Tracings of two records are shown superposed in fig. 4; the pressure records in these two cases were identical. It will be seen that the galvanometer is thrown in slight oscillation by the sudden increase in heating

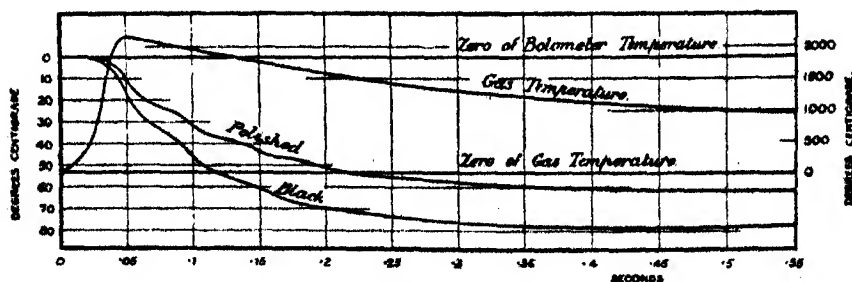


FIG. 4.

when the flame strikes the bolometer. The temperatures of the silver shown in these records after smoothing the oscillations are given in the following table, their ratios being shown in the fifth column:—

Table IV.

Time (from ignition).	Gas temperature.	Bolometer temperatures.		Ratios of temperatures.	Ratios of heat absorbed.
		Black.	Polished.		
0·05	2150	15·9	12·0	0·755	0·755
0·10	1940	45·8	31·9	0·695	0·70
0·15	1750	61·0	44·1	0·725	0·72
0·20	1590	70·0	51·7	0·74	0·73
0·30	1350	76·8	59·0	0·77	0·75
0·50	1030	78·7	62·5	0·795	0·77

In the course of being heated by the flame the silver loses a considerable quantity of heat to the backing with which it is in contact. The percentage of heat so lost depends upon the thermal conductivity and the thermal capacity of the backing, and on the manner in which the temperature of the silver rises. If the two curves for polished and blackened silver were precisely similar, differing only in respect of the scale of temperature, the proportion of heat lost at corresponding times would also be the same for both, and the quantity of heat absorbed would be proportional to the temperature. The curves are not quite of the same shape, and the small correction applicable on this account has been calculated and is allowed for in the last column. The figures there given represent, probably within 5 per cent., the proportion in which the black and polished silver surfaces absorb heat when exposed to gas temperatures varying in the manner shown by the above record. It appears that the mean rate of absorption during the first quarter of a second by the polished surface is 0·74 of the absorption by the blackened surface. The records of pressure obtained with polished and blackened walls, to which reference is made in section (b) above, showed that the mean rate of cooling in a polished vessel during the first quarter of a second was in different experiments from 0·56 to 0·71 of the rate observed when the walls are blackened. The agreement is as good as can be expected, having regard to the great effect of small variations in the state of polish. The bolometer also shows that approximation of the rates of cooling in the two cases as the temperature falls which appeared in the pressure records. The difference in heat absorption represents no doubt the greater part of the radiant heat emitted by the gas in the time, but it does not represent the whole of it. For the black surface is not perfectly absorbent, nor is the polished surface perfectly reflecting. Thus it is quite certain that of the heat given by the gas to the walls of a blackened enclosure during the first quarter-second after maximum pressure, at least 30 per cent. is radiant heat, and the proportion is probably a good deal higher.

The absolute determination of the quantity of heat-loss represented by the rise of temperature of the bolometer strip cannot be effected very accurately, owing to the large proportion of heat lost to the backing. In order to estimate this proportion, the backing may be considered as an infinite solid, the temperature θ of whose plane face is at each instant that of the silver, and is therefore known in terms of the time from the record. Let k and c be the thermal conductivity and thermal capacity per unit of volume respectively of the backing. Then it is easy to show that the total heat which has passed into the backing at time T (reckoned from some moment before the silver began to warm up (say the moment of ignition) is

$$2 \sqrt{\frac{kcT}{\pi}} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt.$$

The proportion which the total heat which has passed into the backing bears to that remaining in the silver ($C\theta_T$) is then

$$\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt.$$

The fraction $\frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt$ is easily obtained graphically for various values of T from the graph of θ , and depends only on the shape of that graph, being independent of the scale to which it is drawn. To complete the calculation of the proportion of heat lost, it is only necessary to find or

estimate the quantity $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$. This might be done by direct measure-

ment of the thermal conductivity and thermal capacity of the backing. The fact that the silver does not cover the whole surface, and that there is a layer of shellac of varying thickness between it and the linoleum, however, introduces a good deal of uncertainty. A more accurate method is to compute the total energy in the gas from its temperature at some time when it has cooled so far that its specific heat may be considered known, and to calculate the total loss of heat at that instant by deducting the energy from the heat developed in the combustion. Comparing this heat-loss with

the heat then accounted for in the silver, a value of $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$ may be found,

which value can be used for computing heat-loss at earlier periods when, from want of accurate knowledge of the internal energy of the gas, it cannot be determined directly. The thermal conductivity and capacity of the backing determined in this way will be effective values of these quantities, in which the various factors of incomplete covering, etc., are taken into account.

Applying this method in the present instance, it has been found that 0.5 second after firing, when the temperature of the gas is 1000°C ., the total heat-loss to the walls (averaged over the whole surface) is 2.5 calories per square centimetre.* The temperature of the blackened silver is then 79°C ., equivalent to 0.93 calorie per square centimetre in the silver. The heat lost to the backing at this epoch is therefore $2.5 - 0.93 = 1.57$ calorie per square centimetre. It is here assumed that the heat absorbed by the bolometer is equal to the average absorption over the whole surface. When $T = 0.5$, we have, therefore,

$$\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \int_0^T \frac{1}{\theta_T} \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt = \frac{1.57}{0.93} = 1.69.$$

The value of the integral is obtained from the record of temperature (see fig. 4), and is found to be 0.895 when $T = 0.5$. It follows that

$$\frac{2}{C} \sqrt{\frac{kc}{\pi}} = 2.7.$$

A direct measurement of the thermal conductivity and thermal capacity of the linoleum, by methods which need not be described here, gave

$$k = 0.00032,$$

$$c = 0.62,$$

whence

$$\frac{2}{C} \sqrt{\frac{kc}{\pi}} = 1.35,$$

or only about half the value given by the other method.

Assuming that $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$ is equal to 2.7, the following table shows the absolute quantities of heat absorbed by the blackened and polished surfaces per unit area at different times. The second column gives the temperatures reached by the two bolometers; the third, the corresponding heat quantities in the silver (calculated on the assumption that the specific heat of pure silver is 0.056); the fourth, the factor $\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt$, which gives the proportion of heat lost to backing; and the fifth, the actual absorption after allowing for this loss. The sixth column is the difference in the heat absorption of the blackened and polished surfaces.

If the absorption by the bolometer is equal to the average over the whole surface of the vessel, the total heat lost to the walls of the blackened vessel at maximum pressure (0.95 second) is 1080 calories, or $6\frac{1}{2}$ per cent. of the whole heat of combustion. This agrees well with the results of experiments

* See Appendix.

Table V.

Time.	Temperatures ° C.			Heat in silver, calories per sq. cm.		Proportion lost to backing.		Total absorption.		Difference calories per sq. cm.
	Gas.	Silver.								
		B.	P.	B.	P.	B.	P.	B.	P.	
0·05	2150	15·9	12·0	0·188	0·142	0·30	0·30	0·245	0·185	0·06
0·10	1940	45·8	31·9	0·580	0·376	0·50	0·50	0·795	0·565	0·23
0·15	1750	61·0	44·1	0·720	0·520	0·70	0·69	1·22	0·88	0·34
0·20	1590	70·0	51·7	0·826	0·610	0·90	0·88	1·57	1·15	0·42
0·30	1350	76·8	59·0	0·906	0·696	1·22	1·18	2·01	1·52	0·49
0·50	1030	78·7	62·5	0·929	0·737	1·70	1·68	2·51	1·94	0·57

in which the resistance of a copper strip completely lining the vessel was recorded.* These experiments showed a total loss of 1200 calories, or 7·5 per cent., at the moment of maximum pressure after the explosion of a 15-per-cent. mixture. The difference between the absorption of the blackened and polished surfaces at this moment would amount to 260 calories for the whole vessel, or about 2 per cent. of the heat of combustion. As already stated, the observed difference in maximum temperature probably corresponds to 5 per cent. in the thermal energy. The balance, which amounts to 2 or 3 per cent., represents a difference in completeness of combustion, in favour of the polished walls.

(2) *Bolometer behind Fluorite Screen.*—A direct measurement of the radiation was obtained by a recording bolometer placed outside the vessel behind a fluorite window. This instrument, which was designed by Mr. W. T. David, is shown in figs. 5 and 6. It consists of a platinum strip (fig. 5) mounted on the end of a hollow wooden cylinder. The strip weighed 0·25 gramme per square centimetre and had a thermal capacity of 0·008 gramme of water per sq. cm. (specific heat assumed to be 0·032).

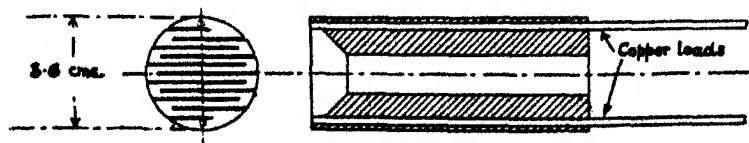


FIG. 5.

The resistance was at first 0·15 ohm, but was reduced in later experiments by short-circuiting two of the coils to about 0·115 ohm (room temperature). The temperature co-efficient was measured and found to be 0·0036. The

* Full details of the method are given in 'Roy. Soc. Proc.,' A, vol. 79, p. 129.

connections of the bolometer were the same as in the experiments last described (blackened and polished silver—see fig. 3). The bolometer, which was blackened with camphor smoke, was pushed into a gun-metal tube screwed into a boss on the end-cover of the vessel, which carried at its inner end the plate of fluorite (fig. 6).

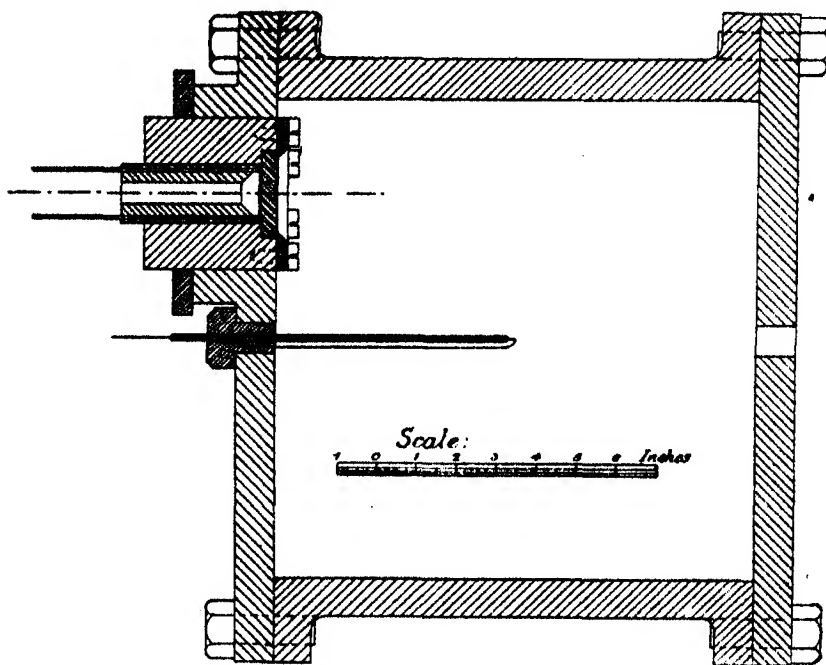


FIG. 6.

The fluorite was $\frac{1}{4}$ -inch thick, and the clear opening $1\frac{1}{2}$ inch diameter. The interior of the vessel was blackened.

One record taken under these conditions during the explosion of 15-per-cent. mixture is reproduced in fig. 7. The figure is an exact tracing from an enlargement of the original. It is noteworthy that there is no oscillation of

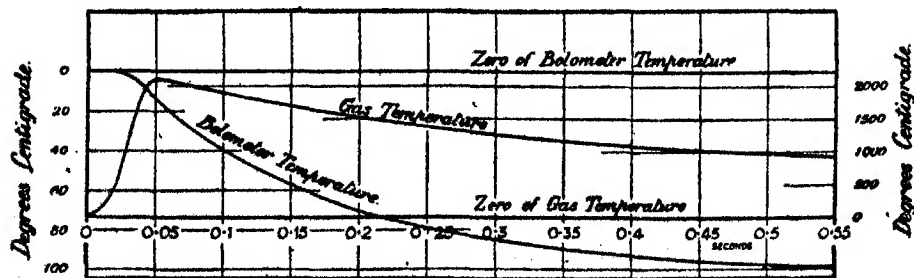


FIG. 7.

the galvanometer, doubtless because there is no sudden heating such as occurs when the flame touches a surface in contact with the gas. The following table shows the results of this record:—

Table VI.

Time from ignition.	Temperature ° C.		Heat in platinum, calories per sq. cm.	Loss.	Total absorbed, calories per sq. cm.	Percentage of heat of combustion.
	Gas.	Platinum.				
0·05	2090	13·6	0·11		0·11	3
0·1	1870	39·6	0·315		0·315	8·5
0·15	1690	57·4	0·46		0·46	12·5
0·2	1510	70·3	0·57		0·57	15·5
0·3	1290	84·2	0·675	0·025	0·70	19
0·4	1110	91·7	0·735	0·035	0·77	21
0·5	980	96·4	0·770	0·05	0·82	22

The loss of heat from the platinum by conduction and radiation (shown in the fifth column) was determined by calculation from the rate of fall of temperature in the later stages of cooling, when no radiation was being received. The percentages in the last column are calculated on the assumption that radiant heat is absorbed by every part of the blackened walls at the same rate as by the bolometer, no allowance being made for absorption in the fluorite or reflection from the bolometer. Probably about 10 per cent. should be added on this account to get the true amount of radiation.

The amount of radiation shown in this experiment is from 40 to 50 per cent. in excess of that given by comparison of the blackened and polished silver bolometer inside the vessel, at corresponding times. The uncertainty attaching to the latter observations, partly because they are difference measurements, and partly because of the very large corrections for loss to the backing, will not have escaped observation. I think, however, that the discrepancy is too great to be accounted for in this way, and that the difference between the absorption by the blackened and polished silver surfaces is really a good deal less than the whole of amount of radiation. Mr. W. T. David has suggested that a film of water may perhaps be formed on the polished surface at an early stage of the cooling and impair its reflecting qualities. About 5 grammes of water are produced in the explosion, and practically the whole of this ultimately condenses on the walls, covering them to an average depth of 1/100th of a millimetre all over, thus destroying in large measure their reflecting power. It is probable that the formation of this layer commences almost as soon as the flame touches the metal, and that a much thinner layer

would be adequate to absorb a considerable fraction of the radiation falling upon it. The fluorite plate, on the other hand, must almost instantly become too hot on the surface to admit of the deposit of moisture. It is possible that the rate of formation of this film depends on the exact state of the metal surface, and that we have here the explanation of the great effect of apparently inappreciable differences in polish on the rate of cooling.

It was found that if a plate of glass was substituted for the fluorite, the heat received by the bolometer was reduced to about one-third; and that if the platinum were polished the heat received was only about 20 per cent. of that recorded with a blackened surface. The latter proportion agrees with the figure given by Hagen and Rubens for the reflecting power of polished platinum.

The experimental work described in this paper has been carried out by Mr. W. T. David, advanced student at the Engineering Laboratory, to whom I am much indebted for the ability and zeal with which he has prosecuted the research and for many suggestions of value. He is engaged upon experiments with the recording bolometer similar to those last described, by which it is hoped to determine the nature and origin of the radiation, and its dependence on temperature and density. The work of R. von Helmholtz* and of Julius† proves that the radiation from a non-luminous flame (*e.g.* a Bunsen flame) burning at atmospheric pressure consists mainly of two bands, of wave-lengths 4.6μ and 2.8μ , which come from the carbonic acid and steam respectively. It is probable that the radiation in a closed-vessel explosion is of substantially the same quality, and Mr. David's work, so far as it has gone, confirms this view.‡

APPENDIX.—*Calculation of Heat-Loss from Pressure Record.*

At 0.5 second from the time of ignition the mean temperature of the gas calculated from the pressure is nearly 1000°C . The energy is shown in the following table:—

* 'Die Licht- und Wärmestrahlung verbrennender Gase,' Berlin, 1890.

† 'Die Licht- und Wärmestrahlung verbrannter Gase,' Berlin, 1890.

‡ It has been suggested that possibly some of the radiation comes from the walls of the vessel, which are heated by the explosion. From consideration of the rate of flow of heat per sq. cm., however, it can be shown that the surface temperature of the metal can never exceed about 40°C ., which is of course quite inadequate to give any appreciable radiation. Further, Mr. David has found that if a patch of the wall opposite the bolometer be highly polished, the radiation received is *increased*. The fluorite plate will be heated to a fairly high temperature at the inner surface, but the radiation emitted by this surface will be absorbed in the fluorite and none of it will reach the bolometer. No appreciable heating of the outer surface can occur during the measurement of the radiation.

Table VII.

Gas.	Volume (gramme-molecule).	Energy 1000° to 100°.
CO ₂	0·09	9000 × 0·09 = 810
H	0·21	8500 × 0·21 = 1370
N	0·70	5000 × 0·70 = 3500
Total.....	1·00	5680

The first factor in the energy of each constituent is the quantity of heat (in calories) evolved by that constituent per gramme-molecule (taken to be 22·25 standard litres in each case) in cooling at constant volume from 1000° to 100° C. These energies are calculated from the results of Holborn and Henning for the specific heat of these gases, but a correction of 5 per cent. has been added in each case because there is reason to suppose that Holborn and Henning's values are too low. The figures are uncertain to the extent of about 5 per cent. The quantity of gas present is 20·3 litres under standard conditions, or 0·905 gramme-molecule (volume of vessel 22·3 litres, pressure before explosion 763 mm., temperature before explosion 16° C., contraction 4 per cent.). Hence the total heat present in the gas (reckoning from 100° C.) at 0·5 second is 5200 calories. The heat evolved by burning the coal gas, taking a calorific value of 115,000 calories per gramme-molecule (580 British thermal units per standard cubic foot, lower value), is

$$0·15 \times 115,000 \times 0·945 = 16,300 \text{ calories,}$$

since the volume before combustion is 4 per cent. greater than after. Hence at this time the total heat which has passed into the walls is 16,300 - 5,200 = 11,100 calories. The total surface of the vessel is 4380 square centimetres, so that the average loss per square centimetre is about 2·5 calories.

The Effect of Small Traces of Water Vapour on the Velocities of Ions produced by Röntgen Rays in Air.

By ROBERT TABOR LATTEY.

(Communicated by Prof. J. S. Townsend, F.R.S. Received May 25,—Read June 9, 1910.)

Some experiments by Prof. J. S. Townsend* on the lateral diffusion of a narrow stream of ions moving in an electric field led to the conclusion that negative ions in perfectly dry air are much smaller than those in air containing a small quantity of moisture. It was consequently to be expected that the complete removal of water vapour would cause an increase in the velocity with which negative ions move under the influence of an electric field of force. At his suggestion the following investigation of the velocities of ions in air at low pressures was undertaken, and it was found that, while the complete removal of water vapour had only a small effect on the velocities of positive ions, yet the same cause increased the velocities of the negative ions by a factor varying between 2 and 30 for the range of pressures and electric forces used in the experiments.

The method adopted was to let the ions travel between two gauzes under a known electric force for a time t and then to reverse the field. If v is the velocity of the ions and d is the distance between the gauzes, then ions starting from one gauze will reach the other if $t < d/v$. If t is gradually decreased, it is possible to find, by means of an electrometer, when ions cease to reach the second gauze; when this happens $v = d/t$.

The ions were generated by X-rays passing through an annular gap between a guard-ring (A, fig. 1) and a thick lead disc (A'), and falling on an annular brass plate (C). By connecting A and C to the poles of an insulated battery (B₁), the ions of one kind can be driven downwards to the gauze which is fastened to C, or driven upwards and discharged by A'.

Below C is a series of concentric rings insulated by ebonite blocks, and between each ring is a coil of a certain high resistance. The lowest of these (D) has a gauze similar to that attached to C. Below this gauze is a brass disc (E), insulated and surrounded by a guard ring in metallic connexion with the base of the apparatus. E is connected to an electrometer.

The gratings, or gauzes, attached to C and to D were carefully constructed of fine brass wire, 0.1 mm. in diameter, and stretched at intervals of 1.0 mm.

* 'Roy. Soc. Proc.' 1908, A, vol. 81, p. 464.

across the opening, so that they did not rise appreciably above the plane of the lower surface of C or the upper surface of D.

A small battery (B_2) attached to D and to the base maintains a P.D. between D and the guard-ring of the same sign as that between A and C.

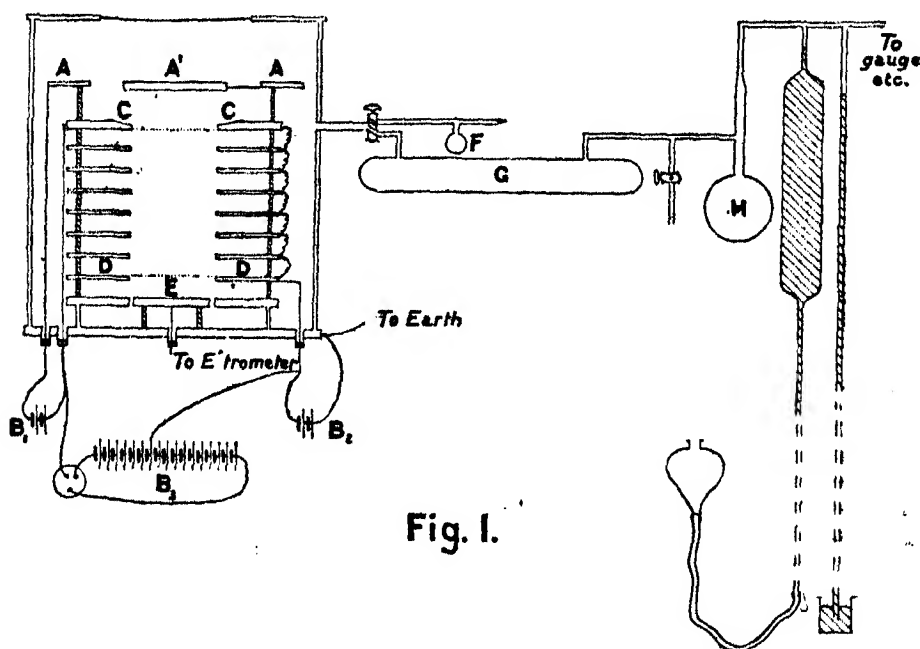


Fig. I.

The ring C is attached to a rotating commutator, by means of which connexion is made for equal periods of time to alternate ends of a large battery of cells (B_1). An intermediate point of this battery is connected to D.

Suppose that a determination of the velocity of negative ions is being made, then A is made negative with respect to C, and D is negative with respect to E and the guard-ring. In this way negative ions are sent downwards into the part of the apparatus between C and D, and any of these which reach D are sent on to E and detected by the electrometer.

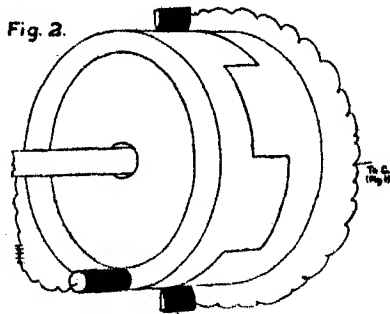
The equal resistances between the rings and the presence of gauzes at C and D ensure uniformity in the potential gradient between these two surfaces. The gauze at D, being at a constant potential, also prevents effects due to induction on E, due to changes in the field between C and D.

The alternating E.M.F. between C and D is made larger in one direction than in the other, so that any ions starting from C which do not reach D while C is negative with respect to D are completely removed during the period in which the field is reversed.

Negative ions coming from the upper grating will therefore move downwards while the first field is on. If they reach the lower grating before the field is reversed their presence will be detected by the electrometer, but if the field is reversed before this has happened the electrometer will be unaffected by them. If, therefore, the commutator is run sufficiently fast, the electrometer should show no deflection; but at a certain speed of rotation, depending on the velocity of the ions and the distance between C and D, a small deflection will be observed.

A brass cylinder, having in its upper surface an aluminium window, was placed over the apparatus. The joints were made air-tight, and a side tube in the brass cover was attached to a two-way tap communicating either with a small bulb F, containing water, or with a tube G, packed with phosphorus pentoxide; this in turn communicated with a T-piece, on one limb of which was a tap by which air could be let into the apparatus, while the third limb was sealed on to a small bulb (H) containing soda-lime and on to an arrangement by which small changes could be made in the pressure of the air. A gauge and a Toepler pump were also connected to the apparatus.

The Commutator.—A heavy brass disc had four equal segments cut away symmetrically from one side, and was mounted on an axle. A similar disc was fastened to this by bolts with insulating washers in such a way that the central part of the rim of the compound disc was formed by alternate portions of the two components. Brushes touching this portion of the rim would therefore make contacts with the right and left halves of the disc alternately (fig. 2). To ensure good contact, two graphite brushes were used at opposite ends of a diameter. The framework of the apparatus was connected to one pole of the battery and a brush touching the insulated disc to the other pole. To ensure smooth running, the small gaps between segments were filled with vulcanised fibre (see fig. 2).



The commutator was tested by connecting one set of segments in series with a battery and voltmeter. When the brush of the commutator rested on one of these segments the voltmeter gave a reading of V , which was reduced to $V/2$ on rotating the commutator, so that the brush must have been in good contact with the segments all the time the commutator was revolving. The number of revolutions per minute was taken either by a speed indicator or by a counter. In this way two values for the time could

be obtained at most speeds. They were found to be in satisfactory agreement.

The commutator was driven by an electric motor and shafting, and its speed could be altered by changing either the resistance of the motor circuit or the ratios of the diameters of the pulley wheels. In this way the time of one revolution could be varied between about 0.65 and 0.02 second.

Method of Experimenting.—The apparatus was exhausted as completely as possible and left overnight. Air was then let in through long tubes packed with soda-lime and phosphorus pentoxide until a suitable pressure was reached. By raising and lowering the pressure regulator the air contained in the apparatus could be drawn backwards and forwards over the pentoxide and so completely dried.

In order to obtain accurate results it is necessary to make two experiments for each speed of rotation of the commutator, in order to eliminate from the charge reaching E the effect due to the few ions which are generated by stray radiations between the gauzes. The deflection δ_1 is found when the force from A to C is in the same direction as that between D and E. A second experiment is then made with the field between A and C reversed, and a smaller deflection δ_2 is obtained, which is due to ions generated below the gauze C. The quantity $\delta_1 - \delta_2$ then represents the deflection due to ions coming through the upper gauze.

Each observation was made by allowing the rays to pass into the apparatus for 30 seconds, and noting the deflection of the electrometer and the speed of rotation of the commutator.

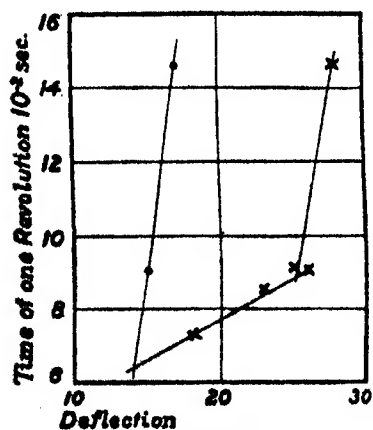


Fig. 3.

The deflections were then plotted on squared paper against the time of one revolution, and by varying the speed of revolution a time could be found for which no additional deflection was obtained due to ions originally starting from C, *i.e.*, a value for T for which $\delta_1 - \delta_2 = 0$ (see fig. 3).

Observations were made both with positive and with negative ions; the positive ions appeared to be but little affected by extreme drying, but with negative ions very large effects were observed.

Positive Ions.—Although the experiments were made alternately with each kind of ion with the same sample of air, yet it seems more convenient to discuss the two kinds of ions separately.

When the gas was very dry it was found that the velocity of the positive ions was directly proportional to the force (X) and inversely proportional to the pressure (p). In fact, vp/X was constant, where v is the velocity.

No.	p (mm.).	X (volts per cm.).	X/p .	v (cm. per sec.).	vp/X .
1	14.3	1.66	0.116	129.6	1116
2		1.785	0.125	144.3	1153
3		2.04	0.143	161.0	1127
4	18.6	1.94	0.104	116.0	1110
5		2.27	0.122	136.5	1116
6		2.53	0.136	151.5	1112
7	24.5	2.53	0.103	112.5	1095
8		2.70	0.110	140.0	1305*
9	28.8	2.70	0.0937	107.0	1140
Mean.....					1121

* No. 8 was omitted in calculating the mean.

This is in accordance with the determinations of other observers who did not take especial precautions to dry the air in their apparatus.

The following are the principal values of vp/X available for comparison :—

Langevin	1105—1076*	Chattock	{ 996 (wet)§
Zeleny	{ 1030 (wet)†		{ 1071 (dry)
	1040 (dry)	Phillips	1060
Wellisch	1170‡	Przibram	{ 908 (dry)¶
			{ 841 (wet)

The values of vp/X found by different observers seem to depend in a small measure on the value of X/p used in their experiments. It is a little difficult to find out from Langevin's papers the actual values of X used by him, but apparently they were such that X/p varied between 0.03 and 1.3; Zeleny used only very small values of X/p (about 0.01 or less).

After admitting moisture to the apparatus the following result was obtained :—

p (mm.).	X (volts per cm.).	X/p .	v .	vp/X .
18.0	2.315	0.1285	101.3	780

* 'Ann. Chim. Phys.,' 1903, vol. 28, p. 514.

† 'Phil. Trans.,' 1900, A, vol. 195, p. 193.

‡ 'Phil. Trans.,' 1909, A, vol. 209, p. 249.

§ 'Phil. Mag.,' 1899, vol. 48, p. 401, and 1901, vol. 1, p. 79.

|| 'Roy. Soc. Proc.,' 1906, A, vol. 78, p. 167.

¶ 'Wien. Ber.,' IIa, 1908, vol. 117, p. 665, and 1909, vol. 118, p. 331 and p. 1419.

The comparatively large effect observed here compared with those observed by Zeleny, Przibram, and Chattock is probably due to the much larger percentage of water vapour admitted in this experiment, since the total pressure was small.

After drawing the air backwards and forwards over phosphorus pentoxide until the gauge had ceased to alter, the pressure had fallen by 1.4 mm. As water was only admitted to part of the apparatus its actual pressure will be greater than this. The ratio of the volume of the whole apparatus to that of the wet part was 1.495. Hence the actual pressure of water vapour will be 2.1 mm., or about 11.5 per cent. of the whole pressure. Now air saturated with moisture at 20° and 760 mm. only contains 2.3 per cent. of moisture. The above experiment was therefore made with about five times the percentage of water vapour used by Przibram.

Negative Ions.—The velocities observed in the case of negative ions in dried air were greatly in excess of those observed by former experimenters. The velocity is apparently a function of X/p which is independent of the actual values of either X or p ; this is shown by the following table of values read off from the smoothed curves drawn for observations made at each of the pressures mentioned :—

p (mm.).	$X/p = 0.04$.	0.05.	0.06.	0.07.	0.08.	0.09.	0.1.
14.3	107	175.5	310	580	1126	(2200)	(4210)
18.4	103	163	279	514.5	1006	(2050)	(4120)
24.5	(119.5)	172.5	286	509	936.5	1799	(3480)
28.8	116	180	298.5	519.5	926	(1652)	
Mean.....	112.5	173.2	287.8	510.5	953.5	1845	3635

The values here given as means were obtained from the smoothed curve drawn after plotting all values of v against X/p . The values in brackets were obtained by extrapolation.

No weight can be ascribed to the apparent slight rise in the value of v when p decreases, since it must be remembered that when $p = 14.3$ mm. and $X/p = 0.08$, then an alteration of 1 mm. in the value of p will change the value of v by about 60 cm. per second, while an error of 0.001 second in determining the time of revolution of the commutator will affect the value found for v by about 40 cm. per second. For velocities over 1000 cm. per second it is necessary to run the commutator at more than 1100 revolutions per minute. There is a possibility that at these speeds contact may not be perfect, and though the contact at high speeds was frequently

checked with a voltmeter, and any results which appeared doubtful rejected, yet there remains a fair margin of possible error in the higher velocities. It should be noted, however, that the sources of probable error indicate that the values given for v are, if anything, too low rather than too high.

The actual values obtained are given in the following table:—

No.	p (mm.).	X (volts per cm.).	X/p .	v (cm. per sec.).
1	14.3	0.60	0.0421	118
2		0.888	0.0621	352
3		1.165	0.0815	1244
4		1.415	0.0990	2670
5	18.2	1.185	0.0651	389
6		1.42	0.0809	1075
7		0.875	0.0471	137
8	18.6	1.16	0.0622	292
9		1.375	0.0740	645
10		1.385	0.0666	239
11	24.5	1.385	0.0566	218
12		1.54	0.0630	339
13		1.76	0.0717	451
14		2.03	0.0829	1120
15	28.8	2.03	0.0829	1340
16		2.33	0.0952	2550
17		1.00	0.0347	90.5
18		1.24	0.0432	134
19		1.715	0.0596	294
20		1.94	0.0677	412
21		2.20	0.0764	800
22		2.30	0.0801	932
23		2.38	0.0826	920

After completing these observations a small quantity of water vapour was admitted, and an observation of the velocity obtained,

$$p = 18.2, \quad X = 2.14, \quad X/p = 0.1107, \quad v = 1302.$$

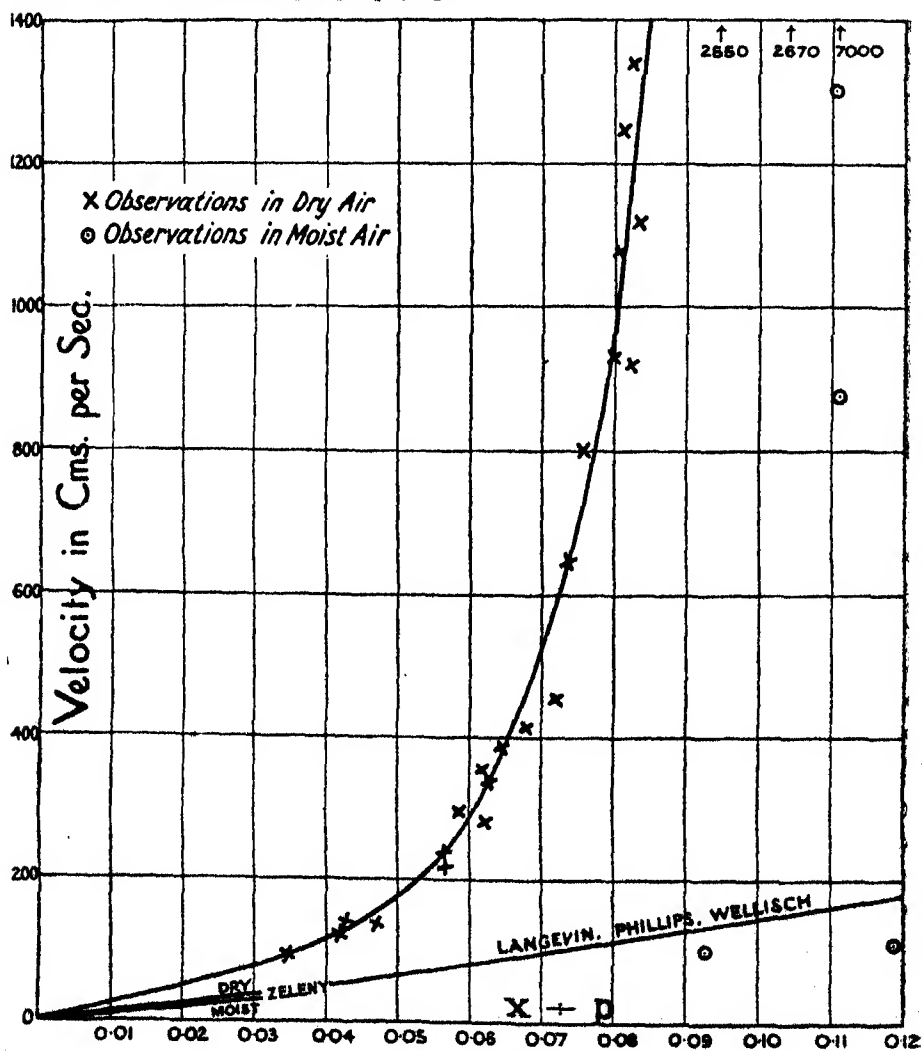
The value of v corresponding to this value of X/p from the extrapolated curve for dry air is about 7500 cm. per second. A small further quantity of water reduced the value of v to 875 cm. per second.

The two-way tap was shut so that no further quantity of moisture could get in and so that communication with the rest of the apparatus was also stopped. The next morning the value of v was observed with the same values of X and p ; it had now risen to 7000 cm. per second, owing, no doubt, to the condensation of moisture on the walls of the apparatus and on the silk covering of the resistances.

A fairly large quantity of moisture was now admitted (about 2.1 mm. pressure, see p. 178), and the following values obtained:—

p .	X .	X/p .	v .	vp/X .
18.5	1.715	0.0927	99.4	1070
19.3	2.30	0.1191	110	924
18.0	2.29	0.127	113	890

The first value was obtained immediately after admitting water, and the other values some hours later. The more complete diffusion of the water vapour through the gas may account for the relatively lower values of these later experiments. All these values, together with those of other observers, are shown on the accompanying graph.



The only values available for comparison with these for ions in moist air are those of Zeleny, who obtained values for $\nu p/X$ ranging from 960 to 1080, but his work was done with values of X and of p very different from those considered here, and the experiments of Przibram, who obtained for $\nu p/X$ the values 1005 in moist air and 1160 in air partially dried by sulphuric acid.

On the Variation with Temperature of the Viscosities of the Gases of the Argon Group.

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(Communicated by Prof. F. T. Trouton, F.R.S. Received May 25,—Read June 9, 1910.)

In continuation of the determinations of viscosity already recorded,* measurements of the temperature variation for the five gases of the argon group have now been obtained. The apparatus used was of the same type as that described in the above papers, with certain modifications to render it suitable for working at different temperatures. Unfortunately, the method is only practicable for a somewhat limited range of temperature. On the one hand, the temperature must be lower than that at which the vapour pressure of mercury becomes appreciable, on account of the very high viscosity of the latter; on the other hand, it must not approach the solidifying point of mercury. At 100° C. the vapour-pressure of mercury is about 1/5 mm. This was judged to be as much as could be safely neglected, and observations were therefore taken at two temperatures only, viz., atmospheric temperature and the temperature of steam. However, although these limitations render observations over a large range impossible, they still allow interesting comparisons to be made of the temperature variations of the different gases. Incidentally, redeterminations of the ratios of the viscosities of the gases to that of air have also been obtained with an entirely new apparatus.

Apparatus.

Fig. 1 represents the apparatus in its modified form. The capillary tube was bent twice as shown in order to reduce the total length of the apparatus

* 'Roy. Soc. Proc.,' A, vol. 83, pp. 265 and 516.

without seriously altering the time occupied by the mercury pellet P in descending. More than 100 cm. of capillary tubing was thus included,

although the distance between the taps Y and Z was rather less than 50 cm. Two small bulbs B_1 and B_2 of about 1 c.c. each were introduced to serve as receptacles for the mercury pellet during the processes of exhausting and filling the apparatus. The total volume between the taps was about 6 c.c. A steam jacket 4 cm. in diameter covered as much as possible of the tubes between Y and Z, a few centimetres only projecting beyond the corks. The tubes passing through the corks were about 1 mm. internal diameter, so that their capacity represented a small fraction only of the whole. The steam jacket was clamped at its middle point and arranged on an axle perpendicular to its length, so that the apparatus could be inverted as desired. A thermometer was inserted for determining the atmospheric temperature only, the steam temperature being calculated from the barometric height.

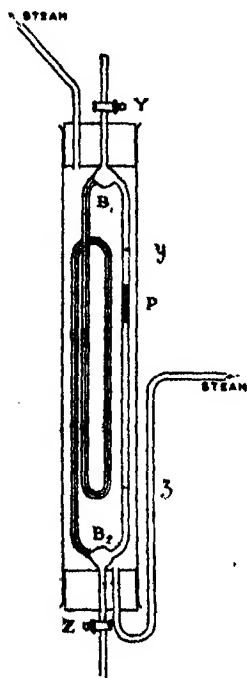


FIG. 1.

The auxiliary apparatus for exhausting and filling was precisely that which has been previously described, no alterations having been found necessary.

Theory of the Method.

It will be seen that the ratio of the viscosities of a gas at two different temperatures is approximately equal to the ratio of the times of fall of the mercury pellet between the marks y and z at those temperatures. Certain corrections, however, must be applied. In the first place, allowance must be made for the expansion of the glass. Meyer's transpiration formula as applied to this method has been shown to take the form:—

$$\eta = \frac{\pi R^4 p t}{8 l v} \left(1 + \frac{4\lambda}{R} \right),$$

where R = radius of capillary tube,

l = length of capillary tube,

p = difference of pressure below and above the mercury pellet,

v = volume between the symmetrically placed marks y and z ,

t = time of fall of mercury between y and z ,

λ = mean free path in the gas.

Of these quantities R , l , v , and p depend upon the expansion of the glass. $4\lambda/R$ is a very small term whose variation in this respect is quite negligible. We may put p in the form mg/A where mg is the weight of the pellet and A is the cross-sectional area of the tube containing it. Hence

$$\eta = K \cdot \frac{R^4 l}{vA},$$

where K is a constant as regards temperature.

Let γ be the linear coefficient of expansion of glass, and θ the temperature difference which causes the viscosity to change from η_1 to η_2 , and the time of fall from t_1 to t_2 . Then

$$\frac{\eta_2}{\eta_1} = \frac{t_2}{t_1} \cdot \frac{(1+4\gamma\theta)}{(1+\gamma\theta)(1+3\gamma\theta)(1+2\gamma\theta)} = \frac{t_2}{t_1}(1-2\gamma\theta).$$

since $\gamma\theta$ is very small.

That is to say, the ratio of the viscosities is less than the ratio of the times in the ratio $(1-2\gamma\theta):1$. Taking $\gamma = 0.000009$ and θ about 84° C., $2\gamma\theta$ becomes 0.0015 , a correction which it is necessary to make.

Secondly, it is necessary to consider whether the variation in mean free path is appreciable. In cases where the pressure remains constant, there is a considerable alteration when the temperature rises from atmospheric temperature to 100° C. But in this case the density and not the pressure remains constant, and a calculation shows that under these circumstances the mean free path increases by only 6 per cent. over the temperature range referred to. Since the mean free path itself only enters the formula as a small correction, so small an alteration in its magnitude is quite negligible.

Consideration was also given to the question of the variation with temperature of the surface tension of mercury. As shown in my first paper* on this method, the unsymmetrical shape assumed by the mercury pellet in descending produces an effective reduction of driving pressure. For tubes of the size used in these experiments this reduction amounts to about 3 per cent. of the whole pressure difference, when the length of the mercury pellet is, as in this case, between 4 and 5 cm. The question is whether this capillary diminution will vary so much with temperature as to make appreciable the effect of its variation on the total driving pressure. The data with regard to the temperature variation of the surface tension of mercury are apparently not very reliable, but for the purpose of applying a small correction the decrease of surface tension for the rise of temperature from 15° to 100° C. may be taken as amounting to about 6 per cent. in the case where air is the superposed fluid. Upon this basis the effective increase of total driving

* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 265.

pressure for the said range would be equal to 3 per cent. \times 6 per cent. = 0.18 per cent. This correction is of the same order as that of errors liable to occur in the measurements; but it has not been applied, owing to the uncertainty of its applicability to cases where gases other than air are in contact with the mercury. It is true that corrections of the same order are applied, as, for instance, that due to the expansion of the glass; but these are perfectly definite and accurately known. It should be pointed out, however, that the values obtained for the temperature coefficients are probably slightly lower than the correct ones owing to this cause. This will be referred to later.

The necessity for the remaining correction appeared during test experiments with air. It was suspected that the exposed portion of the gas enclosed in the apparatus, *i.e.*, that part projecting through the corks, rendered the higher temperature virtually lower than that estimated. To test this point, further experiments were made with the tubes leading to the taps filled with mercury so as to exclude the air. It was then found that the mean time of fall at steam temperature was increased in the ratio 1.0028:1. Since it was not practicable to exclude the gas from the exposed region in this manner when dealing with the rare gases, the mean times of fall at the steam temperature have been increased in the above ratio for the purpose of calculating the temperature coefficients.

Method of Observation.

The apparatus, having been exhausted and then filled with the gas in question, was disconnected from the pump and allowed to stand until the thermometer indicated that the temperature had remained steady for a considerable time. In no case was the variation more than one or two fifths of a degree Centigrade during half-an-hour immediately preceding the commencement of an observation. The times of four falls of the mercury pellet—two in each direction—were then measured. In order to ensure that the whole apparatus was raised to the estimated temperature, steam was passed through the jacket for some 15 minutes before commencing the second set of observations. The passage of steam was, of course, continued throughout. Again four times of fall were measured, two in each direction. By taking the mean in each case the ratio of the viscosities of the gas at the two temperatures could be obtained after applying the corrections mentioned above. It was found that, as in previous determinations, non-uniformity of the tube containing the mercury pellet caused the times of fall in the two directions to differ slightly. Thus the time from y to z was consistently

somewhat greater than that from z to y . However, by taking the mean of equal numbers of falls in the two directions, this effect can be eliminated.

Several determinations were first of all made with air, with very consistent results, the greatest variation in the calculated temperature coefficient being less than 1 per cent. The same mercury pellet was used throughout the whole final series of experiments. This made it possible not only to determine the temperature coefficient for each gas, but also to re-determine the relative values of the viscosities of the different gases.

Experimental Results.

The results of the four determinations made with air were as follows :—

$$\begin{array}{ll} \frac{\eta_{100}}{\eta_{15.4}} = 1.216, & \frac{\eta_{99.8}}{\eta_{15.9}} = 1.214, \\ \frac{\eta_{99.7}}{\eta_{14.5}} = 1.219, & \frac{\eta_{99.9}}{\eta_{16.4}} = 1.212. \end{array}$$

The corrections for the expansion of the glass and for the end error referred to above have been applied in calculating these ratios. The suffixes to η indicate the temperatures. The results indicate that temperature variations of about one-third of a degree are detectable.

In the cases of the rare gases the actual observations will be given.

1.—Helium.—

Times of fall, in seconds.			
Temperature 13°·2 C.		Temperature 99°·7 C.	
<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .	<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .
126·0	125·4	150·8	149·2
126·0	125·2	150·6	149·4
Mean of all = 125·65 seconds.		Mean of all = 150·0 seconds.	
$\frac{\eta_{99.7}}{\eta_{13.2}} = \frac{150.0}{125.65} \text{ approximately.}$			

Applying the necessary corrections,

$$\frac{\eta_{99.7}}{\eta_{13.2}} = 1.195.$$

2. Neon.—

Times of fall, in seconds.			
Temperature 13°·8 C.		Temperature 100° C.	
<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .	<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .
200·6	199·6	237·6	236·4
200·4	199·6	237·4	236·2
Mean of all = 200·1 seconds.		Mean of all = 236·9 seconds.	
$\frac{\eta_{100}}{\eta_{13.8}} = \frac{236.9}{200.1} \text{ approximately.}$			

Applying corrections,

$$\frac{\eta_{100}}{\eta_{13.8}} = 1.185.$$

3. Argon.—

Times of fall, in seconds.

Temperature 16°·0 C.		Temperature 99°·6 C.	
<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .	<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .
143·8	142·0	176·0	174·4
143·6	142·4	175·4	174·4
Mean of all = 142·95 seconds.		Mean of all = 175·05 seconds.	

$$\frac{\eta_{99.6}}{\eta_{16.0}} = \frac{175.05}{142.95} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{99.6}}{\eta_{18.0}} = 1.226.$$

4. Krypton.—

Times of fall, in seconds.

Temperature 16°·3 C.		Temperature 100° C.	
<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .	<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .
161·0	159·8	200·2	198·4
160·4	160·0	199·8	199·2
Mean of all = 160·3 seconds.		Mean of all = 199·4 seconds.	

$$\frac{\eta_{100}}{\eta_{16.3}} = \frac{199.4}{160.3} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{100}}{\eta_{18.3}} = 1.245.$$

5. Xenon.—

Times of fall, in seconds.

Temperature 15°·3 C.		Temperature 100°·1 C.	
<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .	<i>y</i> to <i>z</i> .	<i>z</i> to <i>y</i> .
145·6	145·2	185·4	184·2
146·0	144·6	185·2	184·2
Mean of all = 145·35 seconds.		Mean of all = 184·75 seconds.	

$$\frac{\eta_{100.1}}{\eta_{15.3}} = \frac{184.75}{145.35} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{100.1}}{\eta_{15.3}} = 1.272.$$

The collected results are given in Table I.

Table I.

Gas.	Temperatures.	Ratio of viscosities.
	°C. °C.	
Helium	99·7, 13·2	1·195
Neon	100·0, 13·8	1·185
Argon	99·6, 16·0	1·226
Krypton	100·0, 16·3	1·245
Xenon	100·1, 15·8	1·272

Further, by comparing the times of fall with that in air, the values of the ratio η/η_{Air} , shown in Table II, were obtained. In calculating these ratios, allowance has been made for the different slipping coefficients of the various gases, as described in my previous paper.

Table II.

Gas.	Temperature.	η/η_{Air}
	°C.	
Helium	13·2	1·085
Neon	13·8	1·718
Argon	16·0	1·222
Krypton	16·3	1·362
Xenon	15·3	1·234

Treatment and Discussion of Results.

In order to make exact comparison possible in those cases where previous determinations have been made, it is necessary to assume a law of variation with temperature. It is, of course, not possible to deduce the law from the present measurements, since they only refer to two temperatures. For purposes of comparison, however, the law itself is not of the first importance, provided that the same temperature range is dealt with. As a first approximation we may therefore write

$$\eta_{\theta} = \eta_0 (1 + \beta\theta),$$

where η_{θ} and η_0 are the viscosities at temperatures θ and 0° C. respectively, and β is the coefficient of increase of viscosity with temperature. The ratios given in Table I enable us to calculate β for each of the gases.

The values of β for the four determinations made with air are 0·00266, 0·00267, 0·00266, and 0·00265—mean 0·00266.

The values of β for the rare gases are given in the second column of Table III. It will be noticed that with the exception of the drop from

helium to neon, a rise in atomic weight is accompanied by an increase in the temperature coefficient of viscosity. Thus the latter is by no means proportional to the viscosity itself, since the alternations previously shown to affect the viscosity do not exhibit themselves.

A more usual method of treating the results is upon the basis of Sutherland's* formula—

$$\eta = K \cdot T^{\frac{1}{2}} \left(1 + \frac{C}{T} \right),$$

where T is the absolute temperature, and K and C constants for the gas, the latter depending on the attraction between the molecules. C can be calculated from a knowledge of the ratio of the viscosities of the gas at two different temperatures.

The equation may be written in the form—

$$\eta = \eta_0 \left(\frac{T}{T_0} \right)^{\frac{1}{2}} \left(\frac{C + T_0}{C + T} \right),$$

where η_0 is the viscosity at the temperature T_0 , i.e., 0°C .

The values of C have been calculated by the use of the ratios in Table I alone. In order to obtain η_0 , the absolute value for air obtained by the author, together with the ratios in Table II, has been used. These quantities occupy columns 3 and 4 in Table III.

Table III.

Gas.	$\beta \times 10^3$.	$\eta_0 \times 10^4$ (abs. units).	C .
Helium	2.32	1.879	70
Neon	2.21	2.981	56
Argon	2.83	2.102	142
Krypton	3.08	2.334	188
Xenon	3.89	2.107	252
Air	2.66	1.724	116

The probable error, having regard to the length of time measured, is about 1 per cent. in β , which is equivalent to about 3 per cent. in C ; thus, for example, in the case of helium, β probably lies between 2.30×10^{-3} and 2.34×10^{-3} , and C between 68 and 72.

Comparisons with the results of previous observers may be made with respect to air, helium, and argon. In the case of air the value $C = 116$ obtained in the present measurements is about the average of those deduced from some of the more recent determinations. These values are:—

* 'Phil. Mag.,' 1893, vol. 36, p. 507.

Rayleigh* 111.3, Sutherland† 113, Breitenbach‡ 119.4, and Schultze§ 121.

For helium, Rayleigh|| found $C=72$ as compared with 70, and for argon 150 as compared with 142.

Schultze's¶ values are 80.3 and 169.9 for helium and argon respectively, but this was for a larger temperature range. If Schultze's observations for the range from atmospheric temperature to 100°C . are used for calculating C , it becomes 75 for helium and 156 for argon.

It will be seen that in both cases the values here recorded are somewhat lower than those of Rayleigh and Schultze. It is just possible that the discrepancies partly arise from the cause previously referred to, viz., the slight increase of total driving pressure with rise in temperature, brought about by the diminution of the surface tension of the mercury. For reasons given earlier, the magnitude of this effect was considered too uncertain to justify application. If, however, this were done, the value of β would be increased by about 1 per cent. and that of C about 3 per cent. This would bring up the values of the latter according to the present measurement to 72 in the case of helium and 146 for argon. This still leaves a considerable divergence between Schultze's values and the present ones; but if the comparative difficulties attending the measurement of temperature coefficients over small temperature ranges are taken into consideration, this is not surprising. Similar differences in the value of C obtained by independent observers usually exhibit themselves, as, for example, the variety of values in the case of air quoted above.

Returning to a consideration of the relative values of C for the rare gases, it is surprising to find that it is higher for helium than for neon. According to Sutherland the introduction of C is rendered necessary because gases are not perfect. For a perfect gas C would be zero and the viscosity would vary as the square root of the absolute temperature. Now it is certain that the critical and liquefying points of helium are lower than those of neon; hence, it would be natural to suppose that C_{He} would be nearer zero than C_{Ne} . This, apparently, is not the case, and it seems that in the temperature range considered neon is to be regarded as the nearest approach to a perfect gas known. In the case of the other gases we find what would be expected, namely, that C is high or low according as the critical and liquefying points are high and low. In this connection it is interesting to note that a simple

* 'Roy. Soc. Proc.,' A, 1900, vol. 67, p. 137.

† 'Phil. Mag.,' 1893, vol. 36, p. 507.

‡ 'Wied. Ann.,' 1899, vol. 67, p. 813.

§ 'Ann. der Physik,' 1901, vol. 5, p. 140.

|| 'Roy. Soc. Proc.,' A, 1900, vol. 67, p. 137.

¶ 'Ann. der Physik,' 1901, vol. 6, p. 302, and 1901, vol. 5, p. 140.

relation exists between the value of C and the critical temperature. This will be obvious from the following table, which refers to those of the rare gases whose critical temperatures are known:—

Table IV.

Gas.	C .	T_c (abs.).	T_c/C .
Argon	142	155.6	1.10
Krypton	188	210.5	1.12
Xenon	252	288	1.14

Thus it appears that the constant C is sensibly proportional to the critical temperature. It must be pointed out that this would certainly not apply to helium, where the value $C = 70$ is far larger than the probable critical temperature. Supposing, however, that it does apply to neon, an assumption possibly justifiable in view of the abnormal behaviour of helium referred to above, we should expect the critical temperature of neon to be about 63° absolute.

The existence of the above relation led the author to test its applicability to gases other than those of the argon group. The material available as regards viscosity measurements is very limited, but values are obtainable for hydrogen, oxygen, nitrogen, ethylene, nitrous oxide, and carbon dioxide. In the latter case the values of C obtained by Sutherland and Breitenbach differ considerably—277 and 240 respectively; hence the mean has been taken. For the first three gases the values recorded recently by Schmitt* have been used; the values for ethylene and nitrous oxide are taken from Landolt and Börnstein's tables. The results are as follows:—

Table V.

Gas.	C .	T_c .	T_c/C .
Hydrogen	83	37	0.45
Nitrogen	113	127	1.12
Oxygen	138	154	1.12
Carbon dioxide	259	304	1.17
Ethylene	249	283.6	1.14
Nitrous oxide	260.4	309.9	1.19

Here, again, there is an exception, viz., hydrogen; but, for the other gases, not only is the ratio T_c/C nearly constant, but the constant is the same as for

* 'Ann. der Physik,' 1909, vol. 30, p. 398.

the rare gases. It is to be expected that C , which depends on the mass and dimensions of the molecules, would be in some way connected with the critical temperature; and should the above simple relation be found to be practically universal, considerable additional importance attaches to Sutherland's constant.

I have also made use of the temperature coefficients to re-determine the ratio η/η_{Air} for comparison with the results recorded in my last paper. The values given in Table II are for rather higher temperatures than the earlier determinations. Upon reduction to the same temperatures we obtain results recorded below:—

Table VI.

Gas.	Temperature.	η/η_{Air}	
		Original value.	Present value.
	° C.		
Helium	9.8	1.086	1.086
Neon	10.1	1.721	1.721
Argon	12.8	1.221	1.221
Krypton	10.6	1.861	1.859
Xenon	10.9	1.234	1.231

The agreement is remarkably close, especially in view of the fact that the apparatus used in the two cases was entirely different. This suggests that, at any rate as regards comparative measurements, the method is thoroughly reliable.

The values of the viscosity for the various gases are given in absolute C.G.S. units in Table VII. These are based upon the absolute values for air previously obtained by the author.

Table VII.

Gas.	Temperature.	$\eta \times 10^4$.
	° C.	
Helium	13.2	1.942
	99.7	2.322
Neon	13.8	3.080
	100.0	3.652
Argon	18.0	2.204
	99.6	2.702
Krypton	16.8	2.459
	100.0	3.068
Xenon	15.3	2.222
	100.1	2.827
Air	15.9	1.803
	99.8	2.189

Re-calculation of Relative Molecular Dimensions.

Sutherland, in the paper previously referred to, bases his extension of the simple form of the kinetic theory upon the idea that the mutual attractions between the molecules make collisions more frequent than would be the case with forceless molecules. He shows that this is equivalent to a virtual increase in the cross-sectional area of the molecule, and deduces the important result that the molecules may be regarded as forceless, and hence the simple form of the kinetic theory as valid, provided that the true cross-sectional area of the molecule is imagined increased in the ratio $(1 + C/T) : 1$. In every case where C is known, the true molecular dimensions can be deduced from the virtual ones by the application of this principle. Thus, if α' is the virtual radius, *i.e.*, the value calculated on the simple theory, and α the true radius,

$$\alpha = \alpha' / \left(1 + \frac{C}{T}\right)^{\frac{1}{2}},$$

and the true volume can also be deduced.

I have applied this correction to the relative molecular dimensions recorded in my previous paper. In the following table helium is taken as a standard throughout:—

Table VIII.

Gas.	Relative radius.		Relative volume.		Relative atomic density.	
	New.	Old.	New.	Old.	New.	Old.
Helium	1·00	1·00	1·00	1·00	1·00	1·00
Neon	1·21	1·19	1·79	1·69	2·83	2·99
Argon	1·53	1·68	3·59	4·74	2·81	2·12
Krypton	1·65	1·91	4·53	6·93	4·63	3·00
Xenon	1·83	2·25	6·11	11·37	5·40	2·90

The alterations effected by this correction are very considerable, owing to the large differences in C . I have been unable, up to the present, to discover any simple relations between the various radii and volumes. The size of the atom apparently increases with increasing atomic mass, and, with the exception of the step between neon and argon, there is a general tendency for the density to increase with size. It is, perhaps, also worthy of note that the densities of the atoms of argon and neon are practically identical.

I wish again to express my gratitude to Sir William Ramsay for his kindness in continuing the loan of specimens of these valuable gases for the purposes of these measurements. To Prof. Trouton and Prof. Porter my thanks are also due for much helpful advice.

Additional Refractive Indices of Quartz, Vitreous Silica, Calcite, and Fluorite.

By J. W. GIFFORD.

(Communicated by Prof. S. P. Thompson, F.R.S. Received May 27,—

Read June 23, 1910.)

Reference is made to two previous papers* by the author, the latter in conjunction with the late Mr. W. A. Shenstone, F.R.S., who himself prepared the vitreous silica used.

In these papers the refractive indices of the above substances for 26 wave-lengths are given, and the first of them contains a full description of the special method of measurement adopted.

At the suggestion of Dr. T. Martin Lowry,† seven other wave-lengths of more recent importance have been added, and are now offered. Several of these, especially those in the spectrum of mercury, promise from their extreme brilliancy to be of more than usual value.

The method of measurement employed is identical with that described in the papers referred to; and the same prisms and instruments have been used, as well as a larger goniometer, with telescope and collimator of 30 inches focus, described elsewhere,‡ and used for checking the work. The measure of error is also of the same order, but the figures given point to the greater accuracy of the smaller instrument on which these and previous refractive indices have all been measured.

A table of the additional refractive indices follows:—

Table of Refractive Indices.

Wave-length.	Fluorite.	Quartz (ordinary ray).	Quartz (extra- ordinary ray).	Calcite (ordinary ray).	Calcite (extra- ordinary ray).	Vitreous silica.
6708 Li	1·4322578	1·5414590	1·5504717	1·6536691	1·4842714	1·4560717
6488 Cd	1·4327171	1·5423085	1·5513532	1·6550290	1·4846808	1·4567710
5461 Hg	1·4349895	1·5461684	1·5553393	1·6616473	1·4878900	1·4601545
5086 Cd	1·4361936	1·5482355	1·5574790	1·6652675	1·4895396	1·4619080
4800 Cd	1·4369095	1·5501317	1·5594492	1·6686190	1·4911018	1·4635705
4359 Hg	1·4395206	1·5537988	1·5632274	1·6751756	1·4941037	1·4667412
4046 Hg	1·4415296	1·5571506	1·5667107	1·6813434	1·4969064	1·4696753

* 'Roy. Soc. Proc.,' February 13, 1902, and March 3, 1904.

† 'Phys. Soc. Proc.,' June 25, 1909.

‡ 'Roy. Soc. Proc.,' June 28, 1906.

*The Accumulation of Helium in Geological Time.—IV.**

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received June 4,—Read June 9, 1910.)

There is very special interest in searching among the Archæan rocks for minerals showing a high ratio of helium to radioactive matter. It is here that we might expect to find the strongest evidence that this method of enquiry can afford for the antiquity of the globe: nor is the expectation falsified by results.

Archæan rocks, from their crystalline nature, afford much more choice of minerals than do the fossiliferous formations. A conspicuous example of large helium ratio is already known in thorianite. Several other examples have, however, been brought to light by the present experiments, which show a higher ratio than this substance. I select the most striking of these by way of illustration.

The minerals in question come from crystalline rocks in various parts of the world. Only those from Norway and from North America are, as far as I know, proved by definite evidence to underlie the older fossiliferous formations. In the other cases it is only on general grounds that the same order of antiquity can be presumed.

In striking contrast to the sphenes from Archæan rocks is a sample from the recent volcanic rocks of the Laacher See (No. 1 on list). These are the only sphenes I have examined. The extreme antiquity indicated by the measurements is about 700 million years for Archæan rocks. It must not be forgotten that this is a minimum.

There is one point which requires special discussion. In a paper published in the 'Proceedings,'† I showed that the mineral beryl contained a quantity of helium out of all proportion to its radioactive content. The alternative explanations are—

(1) Beryl might be supposed much older than any other mineral examined. Although the rocks in which beryl occurs are not in general easily dated geologically, this supposition has little plausibility, the more so that many beryls from different localities have shown the same feature.

(2) A much more plausible explanation, suggested to me by Dr. Boltwood,

* For previous papers, see 'Roy. Soc. Proc.' A, vol. 61, p. 272; vol. 82, p. 96; vol. 83, p. 298.

† *Ibid.*, A, vol. 80, p. 572.

is as follows :—Beryl is a substance of extremely peculiar composition. Its crystallisation from the rock magma, which can only contain beryllia at a great dilution, is a process hard to understand, and one about which it would be rash to dogmatise. It is, however, permissible to imagine that one of the longer lived radioactive products, say radium, ionium, or radiothorium, which we know also to be present in the magma, might also be separated by this peculiar crystallisation, in a relatively concentrated form. In a few thousand years such a constituent of the beryl would have lost its activity, and nothing but the helium to which it had given birth would remain recognisable.

If this view is accepted, the question will no doubt be asked, What evidence is there that a similar process has not gone on in the other cases, such as zircon, sphene, or thorianite, relied upon to give a minimum estimate of the age of the rocks in which they occur?

It can only be replied—

(1) Such minerals show a close connection between the helium ratio and the geological age.* As regards sphene, the above table shows the results obtained from a sphene of late tertiary date, which shows a helium ratio quite insignificant compared with *any* of the numerous Archæan specimens examined.

(2) The helium content in cases other than beryl is in close relation to the amount of radioactive matter now present, the ratio being, for instance, of the same order for thorianite as for Archæan sphene and zircon; while the former is a thousand times more active than the latter.

* For evidence of this as regards zircons, see 'Roy. Soc. Proc.,' A, vol. 83, p. 298.

*The Wave-making Resistance of Ships: a Study of Certain
Series of Model Experiments.*

By T. H. HAVELOCK, M.A., D.Sc., Armstrong College, Newcastle-on-Tyne.

(Communicated by Prof. Sir Joseph Larmor, Sec. R.S. Received June 7,—
Read June 23, 1910.)

1. In a previous communication* I proposed a formula for the wave-making resistance of ships, and showed that it expressed certain general qualities of experimental results; further, notwithstanding the limitations of theory and the difficulty of interpretation of experimental data, a good numerical agreement was found in several cases with the published results of tank experiments on models when suitable numerical values were given to the coefficients in the formula.

This paper records the results of a more systematic study of the numerical values of some of the coefficients, the data being taken from certain recent series of experiments; for the present the discussion is limited to those types of model whose resistance-speed curves show clearly the humps and hollows which are attributed to interference of wave-systems originating at the bow and stern. It has been remarked that although the mode of disturbance is different, the action of the bows of a ship may be roughly compared to that of a travelling pressure-point, and further, that the stern may be regarded in the same way as a negative pressure-point.† This point of view originated in the well-known paper of W. Froude‡ on the effect of the length of parallel middle body, and the theory was developed in a later paper by R. E. Froude§; from an inspection of experimental results it was seen that the variations in magnitude and position of the oscillations were in directions which agreed with the above interpretation. On account of the lack of an adequate formula, the available data have not yet been examined numerically in any detail; the present investigation aims at supplying this in some measure. Section 2 is theoretical, with some necessary repetition of previous work; Sections 3 and 4 contain a numerical analysis of some available experimental curves. In Section 5 an attempt is made to estimate the effective horse-power of the "Turbinia," in order to illustrate certain points; while in Section 6 the limitations of the interference theory, in the

* 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 278.

† H. Lamb, 'Hydrodynamics,' 3rd edition, p. 414.

‡ W. Froude, 'Trans. Inst. Nav. Arch.,' 1877, vol. 17.

§ R. E. Froude, 'Trans. Inst. Nav. Arch.,' 1881, vol. 22.

conventional use of the term, are discussed in connection with the residuary resistance curves of finer-ended models.

2. A transverse pressure disturbance travelling over the surface of water at right angles to its axis leaves in its rear a procession of regular waves; on account of the supply of energy needed to maintain this system, there is an effective resistance which may be called the wave-making resistance of the given disturbance. An illustration of a simple type of disturbance, symmetrical fore and aft with respect to its axis, is afforded by the function $P/(p^2 + x^2)$, where Ox is in the direction of motion. The length p may be used to define the distribution of pressure to this extent: when p is decreased, the changes are more concentrated and abrupt, and conversely; we may, as a convention, call $2p$ the effective width b of the disturbance. If the disturbance is made to move with uniform velocity v at right angles to its axis, the height of the waves can be calculated, and thence, from considerations of energy, the corresponding wave-resistance R . If the quantity P which defines the magnitude of the disturbance is supposed an absolute constant, the calculation of R as a function of v gives an expression which rises to a maximum and then diminishes ultimately to zero with increasing values of the velocity.* But if the pressure disturbance is associated with a moving ship, it seems reasonable to suppose that P depends upon the velocity, and in fact the assumption is that P varies as the square of the speed.

In this way we obtain the result

$$R = B e^{-bg/v^2}. \quad (1)$$

where B is independent of v . According to this expression, R increases from zero up to a limiting value B ; at any given speed R is a certain fraction of the value B , and if the quantity b were increased the same value of R would only be reached at some higher speed. Further if we have a second expression R_1 with constants B_1, b_1 , greater than B, b , respectively, the curve for R_1 will intersect the curve for R at a certain velocity; at lower speeds $R_1 < R$, while at higher values $R_1 > R$.

Suppose now that a similar negative pressure system, with a different coefficient P , but with the same width b , is situated behind the first system, with a fixed distance l between the two axes. The wave-making resistance of the combined system is given by an expression $\beta(1 - \gamma \cos gl/v^2)e^{-bg/v^2}$, where β and γ are independent of v . In applying this result to the case of a ship, we can of course only expect agreement if the type of model is such that we may imagine distinct, but mutually interfering, wave-systems originating at the bow and stern; it is, in fact, an attempt to describe the wave-making

* Cf. Lord Kelvin, 'Math. and Phys. Papers,' vol. 4, p. 396.

properties of a ship in terms of the coefficients of a simple equivalent pressure distribution of the type specified. Another point which must be noted is that the previous expression is obtained by considering two-dimensional motion only; but the bow and stern of a ship act more like point disturbances than as transverse line systems, hence there are diverging, as well as transverse, waves. In default of a fuller analysis, I have suggested for certain reasons the addition to R of a term $\alpha e^{-b\gamma/90^\circ}$; it is retained for the present, because it indicates the necessity for some expression of the diverging waves and it agrees with certain general properties of them, and also in several cases it allows us to obtain better numerical agreement at lower speeds.

We suppose that R is expressed in pounds per ton displacement of the ship, also V is the speed in knots, L the length of the ship on the water line in feet, and c is equal to V/\sqrt{L} ; then we have

$$R = \alpha e^{-\frac{m}{c^2}} + \beta \left(1 - \gamma \cos n/c^2\right) e^{-\frac{m}{c^2}} \text{ lbs. per ton,} \quad (2)$$

where $m = 11.3b/L$ and $n = 11.3l/L$.

In the following examples attention is directed chiefly to the variations of β and m , and incidentally to those of γ and n . The length b cannot be taken directly as the length of the entrance or run of the ship, for it will depend also on the lines of the model; but one may expect the ratio b/L to decrease as the slope of the model at the bow is increased, and conversely; similarly the number n will vary in a direction which may be predicted. In the previous paper sufficient agreement was found when m and n were assigned fixed values; in many cases the mean curve of residuary resistance appeared to have a point of inflection near $c = 1.3$, and for this we had $m = 2.53$; further, the humps and hollows agreed with $n = 10.2$ for the angle n/c^2 in radians, or $n = 584$ for the angle in degrees. With none of the coefficients fixed beforehand, it is necessary to adopt some method of approximation. Drawing the experimental curve of residuary resistance on a suitable scale, a fair mean curve was sketched in and an equation $R = Ae^{-m/c^2}$ was found, generally by graphical methods, to fit this as closely as possible; in fact it was the original intention to limit the study to the two leading coefficients A and m so determined. The value of m is now fixed, and from the intersections of the mean curve with the actual oscillating curve one could assign a value to n with sufficient accuracy. Finally the three remaining quantities were found from three points on the actual curve, for example, at $c = 0.6, 1.2, 1.8$, if the curve extended so far. In practice the lowest point determines α , for the term in β is negligible there; for the same reason the values of β and γ are more satisfactory when fairly high values of c are available. In all cases the

approximation was not carried further than the circumstances seemed to warrant; the values of the coefficients are given generally in round numbers, and the theoretical curves were calculated throughout their range from the formulæ so obtained.

3. The first series is taken from a paper by D. W. Taylor* on the influence of the shape of midship-section upon the resistance of ships; from the curves in that paper I have taken four, which form a series having the same midship-section coefficient, but with different displacements. The data and the results are given in the following table:—

Table I.—Models I to IV.

No.	Displacement in lbs.	Displacement-length coefficient.	Beam.	Draft.	α .	β .	γ .	m .	n .
I	500	26.6	1.865	0.467	1.6	81	0.14	2.7	564
II	1000	53.2	1.980	0.660	2.0	160	0.18	3.0	540
III	1500	79.8	2.364	0.809	2.0	240	0.18	3.2	540
IV	2000	119.7	2.895	0.991	2.5	360	0.18	3.5	540

Cylindrical coefficient = 0.68; midship-section coefficient = 0.90;
water-line length = 20.51 feet; beam/draft = 2.928.

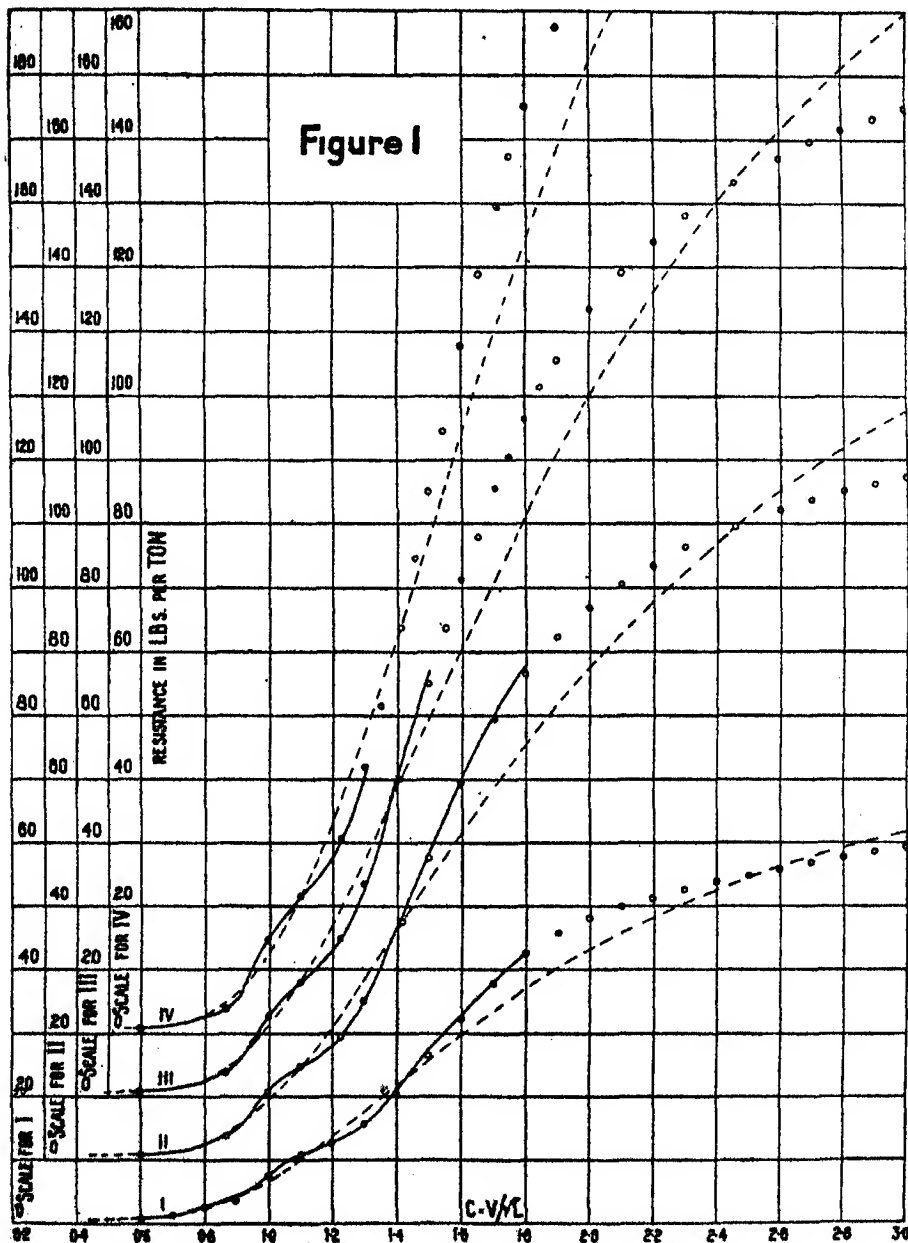
The curves in fig. 1 indicate the results of the analysis; in each case the continuous curve is the experimental curve of residuary resistance; the points marked by circles have been calculated from the formula (2), while the broken curve is a mean curve graphed from the expression $\alpha e^{-m/c^2} + \beta e^{-n/c^2}$. The calculated curves have been extended as far as $c = 3$, in order to include the highest theoretical point of intersection of the mean and oscillating curves.

The third column in Table I refers to a coefficient of fineness used by Taylor in the paper referred to; it is defined as $D/(L/100)^3$, where D is the displacement of the model in salt water in tons, and L is the water-line length in feet. It is a method of estimating the proportions of a model by the displacement of a ship of the same lines and of 100-foot length.

From the numbers in Table I, β appears practically proportional to the displacement. The resistance R has been calculated in pounds per ton displacement, so that dimensionally β is a pure number. In this series certain quantities are constant, namely, with the ordinary notation, L , B/H , $(B \times H \times L)/D$, and (area of midship-section)/($B \times H$). As far as this series is concerned we might regard β as proportional, for instance, to $(B \times H)/L^3$ or to the displacement-length coefficient.

* D. W. Taylor, 'Trans. Amer. Soc. Nav. Arch.,' 1906.

The index m of the exponential increases slightly with the displacement, that is, with increasing beam and draft; this variation is in the direction



one might anticipate, as it indicates a greater diffusion of the pressure changes. In regard to the coefficients specifying the interference between

the bow and stern systems, γ is larger at the higher displacements, while n is less; both variations are consistent with a diminution of the distance between the axes of the simple equivalent pressure distributions.

To illustrate the smaller changes which are possible at the same displacement, three models are taken from the same paper, having different midship-section coefficients with the same area of midship-section; thus smaller coefficients are associated with greater beam and draft. One of these three is No. 1 of Table I: midship-section coefficient = 0.9, $\beta = 81$, $m = 2.7$. Another of the set I had already used in my previous paper with the results: midship-section coefficient = 0.7, $\beta = 82.5$, $m = 2.53$. For the third of the series the same coefficient is 1.1, and there is a good agreement by taking $\beta = 79.5$, $m = 2.87$.

4. The next sets of experimental results are taken from a paper by D. W. Taylor* on the influence of length of parallel middle body. One must notice that the problem investigated is not quite the same as in the paper by W. Froude referred to above. In the latter case the bow and stern of the model were unaltered, but varying lengths of parallel middle body were inserted between them, so that the special effect was isolated as far as possible. In Taylor's experiments the models have constant length and displacement, but varying proportions of the length are occupied by a parallel middle body, and, of course, the bow and stern vary in form so as to keep the displacement constant; the effect is thus more complex theoretically. We may anticipate the direction of variation of some of the coefficients with increasing percentage of parallel middle body under these conditions. Since the ratio of the length of entrance and run to the length of the ship becomes less, the index m should decrease; also the effective distance apart of the bow and stern systems becomes greater, so at the same time γ should decrease and n increase.

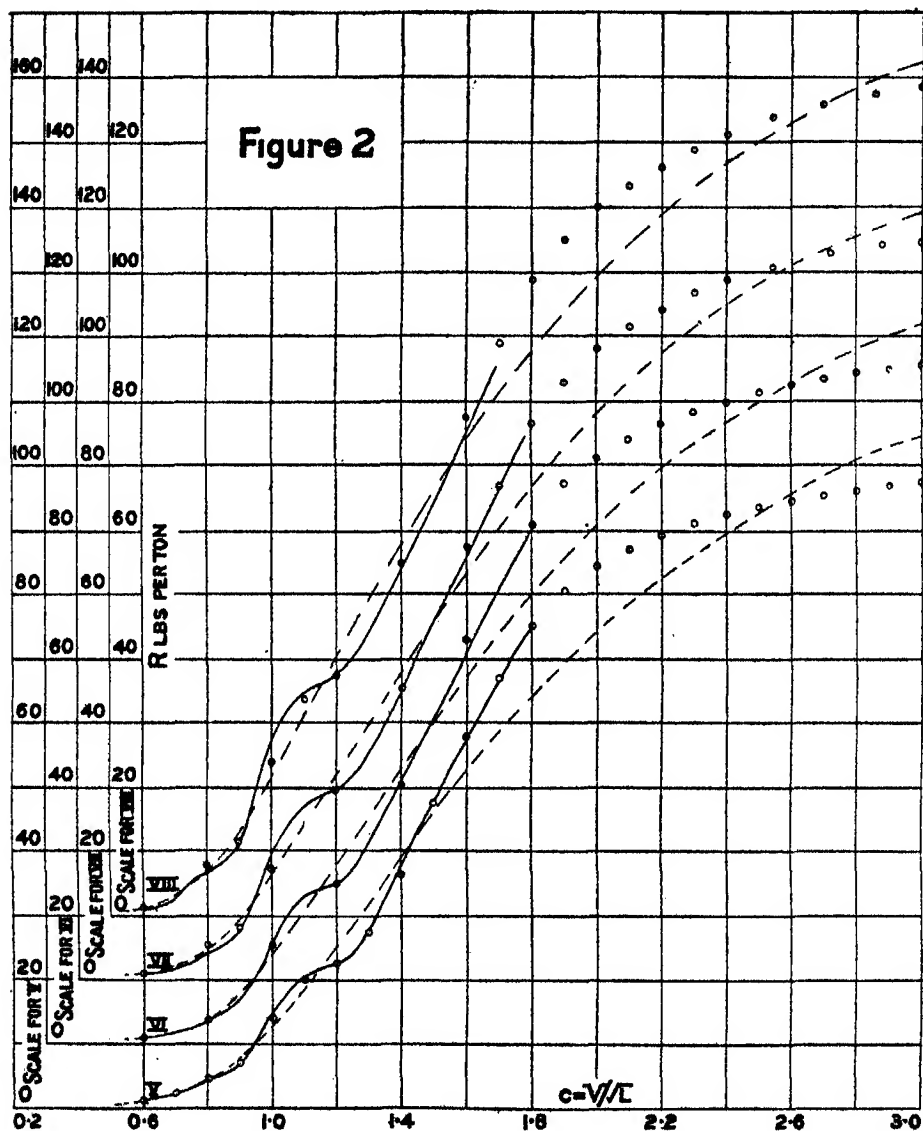
Table II.—Models V to VIII.

No.	Percentage of parallel middle body.	Cylindrical coefficient of ends.	α .	β .	γ .	m .	n .
V	0	0.740	2.5	185	0.17	2.53	584
VI	24	0.688	2.0	145	0.16	2.45	584
VII	36	0.594	2.0	155	0.14	2.35	605
VIII	48	0.500	2.0	165	0.12	2.10	650

Displacement = 1000 lbs.; length = 20.51 feet; beam = 1.682; draft = 0.673; displacement-length coefficient = 53.2; midship-section coefficient = 0.96; beam/draft = 2.5.

* D. W. Taylor, 'Trans. Amer. Soc. Nav. Arch.', 1909.

Table II contains the results for a set of four models of 1000 lbs. displacement, together with other data; the corresponding curves are shown in fig. 2 in the same manner as before.



From the curves in fig. 2, it will be seen that the calculated curves express the general variations in the manner anticipated above. The numerical agreement is best throughout the range for Model V, while for the other curves the agreement at lower values of c is not so good; this appears to be

associated with the change in shape of the ends of the model. Although for the whole length of each model the cylindrical coefficient is 0.74, on account of increasing proportion of parallel middle body the ends become finer; this is indicated in the third column of Table II. The formula (2), in its present form, gives best numerical agreement for models with fuller ends, that is, with fairly high cylindrical coefficients; this point is examined further below.

The same remarks apply to a second set of four models, taken from the same paper, having a displacement of 1500 lbs. The results are given in Table III and the curves in fig. 3. For Curve XII, a point in connection with the interference-coefficients γ and n may be noticed. Whatever value of n is used, if the simple theory is to be adequate, there must be certain relations between the values of c at which the humps and hollows occur; beginning with the highest values and working down to lower speeds, the successive values of c at which hollows, humps, and mean values occur must be proportional to the reciprocals of the sequence

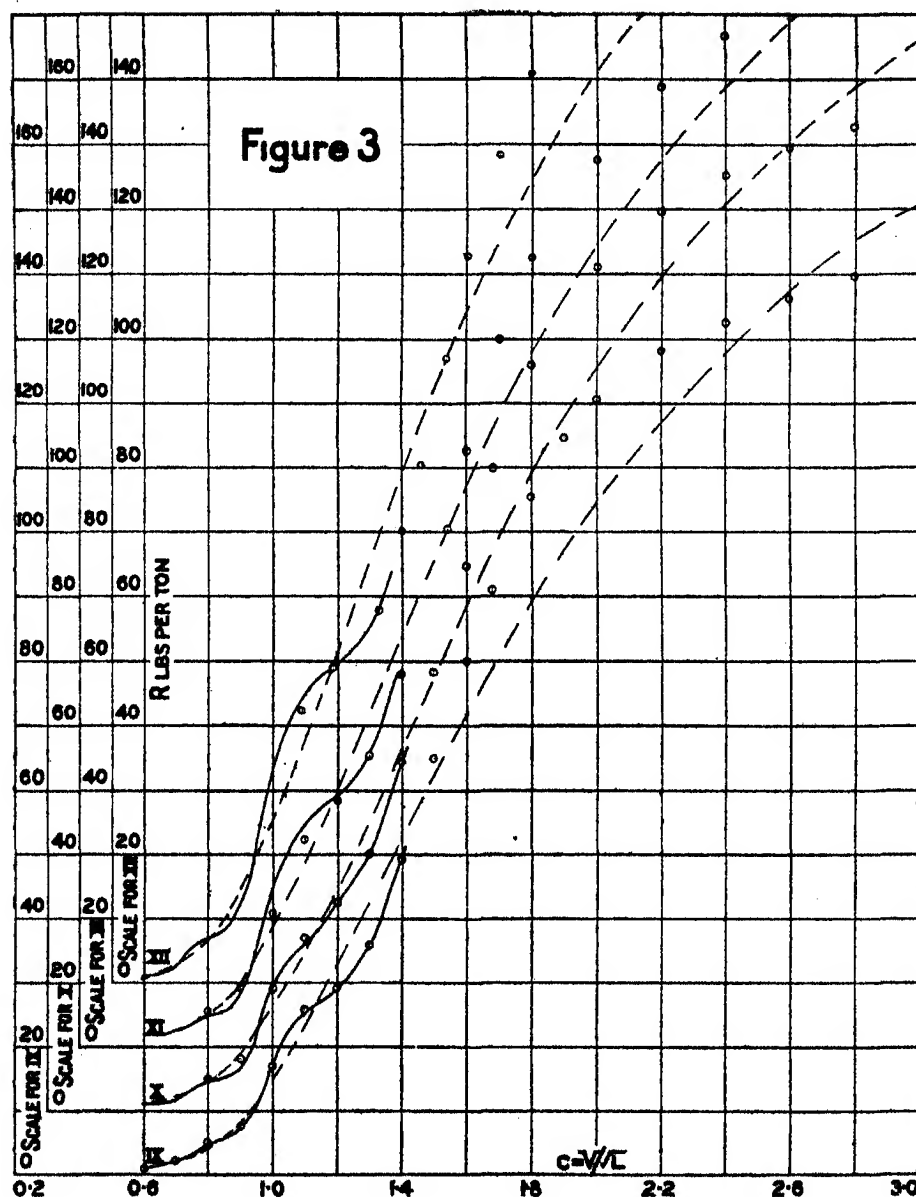
$$\sqrt{0}, \quad \sqrt{0.5}, \quad \sqrt{1}, \quad \sqrt{1.5}, \quad \sqrt{2}, \quad \sqrt{2.5}, \quad \dots\dots$$

In all the curves given here the graphs have been extended to $c = 3$, so as to include, in most cases, the highest mean value, corresponding to the second term in the above series. In most cases it was possible to choose n so that this relation was approximately satisfied, but the difficulty increases apparently at higher displacements, such as in Model XII. The mean curve shown for this case in fig. 3 represents the curve $R = 255c^{-2.3/c^2}$; determining the value of n from the intersections of this with the actual curve, the numbers obtained from the higher positions are larger than those from the lower speeds. In consequence, the circles showing the theoretical continuation of the curve have been calculated with $\gamma = 0.15$ and $n = 610$, without attempting a fit over the whole curve.

Table III.—Models IX to XII.

No.	Percentage of parallel middle body.	Cylindrical coefficient of ends.	α .	β .	γ .	m .	n .
IX	0	0.740	2.5	200	0.19	2.7	584
X	24	0.658	2.2	210	0.17	2.64	584
XI	36	0.594	2.0	235	0.14	2.6	610
XII	48	0.500	—	255	—	2.8	—

Displacement = 1500 lbs.; length = 20.51 feet; beam = 2.060; draft = 0.824; displacement-length coefficient = 79.8; midship-section coefficient = 0.96; beam/draft = 2.5.



5. The curves in the previous sections have been examined chiefly from a theoretical point of view, that is, with the object of testing in these cases the general adequacy of a certain type of simple equivalent pressure distribution. One might try also to classify the coefficients of the formula, so as to obtain empirical expressions for them in relation to the form of

the model. The latter is frequently specified by various coefficients of fineness, which of course give only an approximate estimate of form, and in any case do not make a set of independent variables; no attempt is made here beyond giving all the available data for each model. With the results given above and in the previous paper, one can find an approximate estimate of the leading coefficient β , at least for forms similar to those already examined. It was noticed that, other things being equal, β was proportional to the displacement-length coefficient; also for given values of the latter β appears to be approximately proportional to the ratio of beam to draft. This seems reasonable, since wave-making is largely a surface effect; that is, for a disturbance travelling below the surface the wave-making falls off rapidly with its depth. In several of the cases already examined, it happens that β is numerically only slightly larger than the product of the two ratios mentioned, that is, β is a little greater than $(B/H) \times D/(L/100)^3$, with all the quantities in the units specified above. This result is used now to make an approximate estimate of total effective horse-power for a certain ship, as it affords opportunity for introducing other points of interest. The data for the ship are those of the "Turbinia," as far as they are available from the published record of trials.*

Turbinia.—Displacement = $44\frac{1}{2}$ tons; length = 100 feet; beam = 9 feet; draft = 3 feet; cylindrical coefficient = 0.66; speed = 31 knots.

The displacement-length coefficient is 44.5, while the ratio of beam to draft is 3; since the cylindrical coefficient is less than those already examined, we take β as about 5 per cent. greater than the product of these two ratios, that is, $\beta = 140$. Following out the indications of the previous cases, m should be nearly 3; as we shall calculate quantities for $c = 3.1$ the exponential e^{-m/c^2} only varies slowly with m , so that $m = 3$, with sufficient approximation. Under the same conditions we take $n/c^2 = 60^\circ$ and $\gamma = 0.15$, also $\alpha = 2$. Calculating from formula (2) with these values, we obtain an estimate of 410 for the effective horse-power of the ship at 31 knots due to wave-making, with the possibility of this being slightly in defect; any of the usual approximate formulæ, with simple powers of the speed, when extended to this high value of c give possibly twice this estimate, a result which is much too high. If we take the area of wetted surface (S) as 970 square feet and the frictional coefficient (f) as 0.0095, we may calculate the frictional effective horse-power from the expression $0.00307fSV^{2.83}$; it is 470 at 31 knots. We obtain thus an approximate estimate of 880 for the total effective horse-power of the ship at 31 knots. It is stated in the record referred to above that the total effective horse-power at 31 knots is 946,

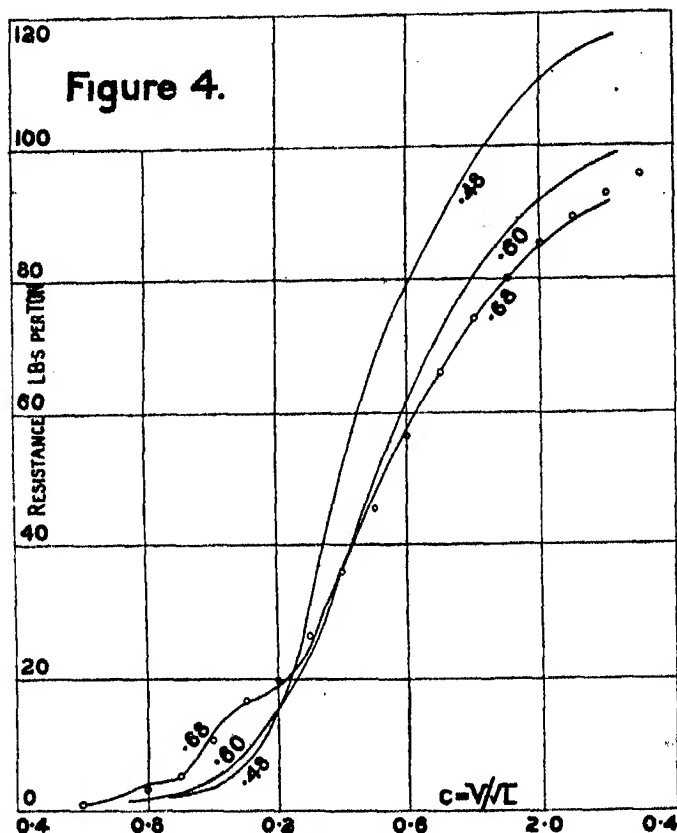
* C. A. Parsons, 'Trans. Inst. Nav. Arch.,' 1897, vol. 38, p. 232.

obtained by Froude's method from tank experiments on a model of the ship; no details of the calculation are given. Although the estimate above is only approximate, another possible factor should be noted; this is the influence of the finite depth of the tank. It has been stated that, from recorded experimental data, this effect becomes appreciable when the length of the waves exceeds twice the depth; this means approximately when $c > 1.9h/L$, h being the depth of water and L the length of the model. This appears to agree with the curves of fig. 11 of my previous paper, which were obtained from theoretical considerations. The effect of shallow water is an excessive increase in the resistance for a considerable range, but if the speed is made high enough the resistance may become even less than in deep water at the same speed. It seems possible that the tank experiments quoted above come within the range of excess of transverse wave-making resistance. It is stated that, assuming a propulsive coefficient of 60 per cent., the value of 946 means a corresponding indicated horse-power of 1576; it may be noted that the estimate of 880 corresponds to the same indicated horse-power with an efficiency of about 56 per cent. In this connection the following remark may be quoted from a recent discussion: "Is it possible that this is one contributing cause to the large propulsive coefficients obtained by torpedo craft compared with those obtained in full-sized vessels, viz., that the tank effective horse-power of torpedo craft models is over-rated, because of excessive transverse wave-making resistance in the 'shoal water' of the tank" ?*

6. It must be noted that all the preceding calculations refer to rather full-ended models, that is, with a cylindrical coefficient of about 0.68 and upwards. It was upon such a type that the original experiments of Froude were performed, and it seems that the characteristic interference effects occur specially in such vessels; the latter are associated with the idea of two fairly distinct systems of pressure disturbance at bow and stern respectively. Now if the ends are made finer it is reasonable to imagine the two systems coalescing into what could be more accurately interpreted as one pressure system. This would be more diffused over the length of the ship, so the equivalent index m should be larger; further, since for constant displacement finer ends mean larger beam and draft, the limiting coefficient β should be larger. Consequently, for decreasing cylindrical coefficient, at constant displacement, the curves of residuary resistance should be intersecting curves, lower at low speeds and then ultimately higher. This is illustrated in the curves in fig. 4, which have been superposed to show the point in question. The curves are taken from a series of 1000-lb. models by D. W. Taylor, of

* E. Wilding, 'Trans. Inst. Nav. Arch.', 1909, vol. 51, p. 160.

constant midship-section coefficient 0.928, and with the ratio of beam to draft 2.923; the cylindrical coefficients are 0.68, 0.60, and 0.48.



The curve with a coefficient of 0.68 is represented quite well by formula (2) with $\alpha = 2$, $\beta = 155$, $\gamma = 0.14$, $m = 2.9$, $n = 584$; the circles represent calculated points. The typical oscillations are clearly visible in this curve, but they appear to be absent altogether from the other two curves; the general character of the latter curves is in accordance with the remarks made above. One may even obtain some numerical agreement with γ zero and larger values of β and m , but it is unsatisfactory without a further examination of intermediate stages and their equivalent pressure distributions; another point is that with a larger value of m the first term in the formula, which represents the diverging waves, becomes more important, and adds another reason for deferring the study of finer-ended models.

Dispersion of Light by Potassium Vapour.

By Prof. P. V. BEVAN, Royal Holloway College.

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[PLATE 2.]

Anomalous dispersion in the region of the red lines of potassium was first observed by Ebert* in 1904. The method adopted for Ebert's experiments was a modified form of the crossed prism method used by Wood in the investigation of the corresponding phenomena in the case of sodium. Potassium was heated in a tube through which two currents of hydrogen passed from each end to a central outlet. The cool hydrogen kept the potassium vapour in a prismatic form, so that light passing along the length of the tube suffered deviation and dispersion by the potassium vapour prism. The author of the present communication has shown† that there is no need for the hydrogen streams. If the tube be kept cool on its upper surface the metallic vapour takes of itself a prismatic form or is arranged in layers of decreasing density, and so behaves in a similar way to a prism of homogeneous vapour. The present communication deals with quantitative results from the measurement of dispersions at different wave-lengths, and it appears that the deviation due to potassium vapour is observable over the whole of the visible spectrum and for a considerable distance in the ultra-violet. Strong absorption takes place at the lines of the principal series and for wave-lengths near these series lines we have "anomalous" dispersion. This phenomenon has been observed at seven of the pairs forming the principal series lines for potassium—as the pairs of lines in this series get closer and closer together with diminishing wave-length, the dispersion effects after the first two pairs are only observable outside the lines forming a pair, but there appears a lack of symmetry in the observed dispersion curves corresponding to the different intensities of the lines forming the pair. The dispersion to be observed may then be regarded as that corresponding to the principal series absorption lines; no other absorption region seems to affect the dispersion—at any rate at low densities of vapour.

The method of experiment was the well-known method of Wood for similar experiments in sodium vapour. Some metallic potassium was placed in a steel tube about 70 cm. in length and 3 cm. in diameter. The ends of the tube were jacketed by concentric brass vessels through which water

* H. Ebert, 'Boltzmann-Festschrift,' 1904.

† 'Phil. Mag.,' 1909, vol. 18, p. 407.

could be passed to keep them cool. The tube was closed at each end with a quartz plate. A side tube was soldered to the main tube, which could thus be connected with an air pump or a supply of hydrogen. An open brass trough with its bottom formed to fit the steel tube could be placed on the top of the steel tube, and cold water could be kept continuously running through this. The under side of the tube could be heated by a row of bunsens or other suitable burner. Wood has put forward the view that the dispersion is due to the layers of vapour decreasing in density from the bottom upwards, and not to the vapour forming a nearly homogeneous prismatic mass about a piece of the metal. I am inclined to think that the latter is, however, the true view. The best results are obtained with a low pressure of gas in the tube, and it is difficult to see how there can be much difference in density of vapour in the tube unless there is very rapid evaporation of the metal going on. But under the conditions when the dispersion is observable the metal is evaporating extremely slowly—a tube can be used for many hours with practically no observable distillation. It seems more probable that there is in the metallic vapour itself very little temperature gradient, and that we get a surface at which condensation of the vapour takes place, and small drops of liquid metal are formed which fall back into the original metal. This view is supported by the fact that I have been able to obtain the sharpest and steadiest dispersion curves in the spectroscope when only a small portion of the tube is heated. I find that heating a larger portion adds little to the deviation but considerably to the absorption. Whatever the actual state may be, the vapour behaves like a prism and deviates light sent through it. Light from a horizontal slit illuminated by an arc lamp was sent through the vapour tube and then focussed by a lens on the vertical slit of a spectrograph. The lens used for focussing this image of the slit was, I believe, a new kind, and proved very useful, so that it may merit a short description. An ordinary quartz lens is troublesome because of the difficulty of focussing for light of different wave-lengths. Achromatic combinations of quartz and fluor spar have been made, but their expense makes them not available for ordinary use. The lens used for these experiments was a combination of quartz and water. Distilled water is transparent for ultra-violet light to wave-length 2000 Ångström units to nearly the same extent as quartz. A layer of water 1 cm. thick absorbs 9.2 per cent. of the light at wave-length 2200, 9.8 per cent. at 2100, and 14.2 per cent. at 2000.* A plate of quartz of the same thickness absorbs 5.8 per cent. at 2220, 8 per cent. at 2140, and

* Kreusler, 'Annalen der Physik,' 1901, vol. 6, p. 412.

16·4 per cent. at 2030.* After standing for some time in glass vessels, water loses a good deal of its transparency, but it is still very transparent until a wave-length of 2100 is reached. An advantage that a water diverging lens has is that it may be made as thin as one chooses near its centre, so that the proportion of light absorbed can be made very small.

The scheme adopted for the lens was to make a thin cell consisting of a parallel plate of quartz and a quartz lens with surfaces of appropriate curvature. These two quartz cell walls were fixed together with shellac to a very short wide brass tube so that the convex face of the lens was nearly in contact with the quartz plate. We thus have a plano-concave water lens when the vessel is filled, which with the convergent quartz lens can give an achromatic combination by suitably choosing the radius of curvature of the outer surface of the quartz lens. A better combination would be to have the vessel made with walls of two similar quartz lenses, one dextro-rotatory, the other levo-rotatory, to eliminate the double refraction effect introduced by the rotatory power of the quartz. It is easily shown that for such a combination to be achromatic for wave-lengths for which the indices of refraction are μ_1, μ_2 , for quartz, and μ'_1, μ'_2 , for water, the radii of curvature of the surfaces r, s , must be related by the equation

$$\frac{r}{s} = \frac{\mu_1 - \mu_2}{\mu_1 - \mu_2 - (\mu'_1 - \mu'_2)},$$

and then r divided by the focal length of the combination is

$$\mu - 1 - \frac{r}{s}(\mu - \mu')$$

for a wave-length for which the refractive indices are μ for quartz and μ' for water.

If we choose the ratio r/s so that the combination is achromatic for wave-length 2570 and 3940, we find this ratio is 4·759. Taking for this ratio 4·75, we do not introduce much error, and have a number more convenient for the actual grinding of the lens. The lens is thus a concavo-convex lens, and the convex side has to be in contact with the water. For the combination of two quartz lenses, two with the same radii of curvature will, of course, give a combination of double the power of the single one.

With the value 4·75 for r/s , we find for r/F , F being the focal strength of the combination, the following numbers:—

Wave-length.....	2190	2310	2570	3400	3940	4670	5890
r/F	0·447	0·451	0·460	0·463	0·460	0·458	0·457

From 2570 to 5890 the focal length is thus very nearly constant, and the change in focal length down to 2190 is not very large. We have thus a

* Pfüger, 'Physik. Zeitschr.', 1904, vol. 5, p. 215.

very nearly achromatic combination for light from the D lines to 2570 in the ultra-violet, and the chromatic effects will not be noticeable down to wave-length 2190. If we compare these results with the values of $\mu-1$ for quartz, which is, of course, proportional to the reciprocal of the focal length of a quartz lens, we see the great improvement, for in the case of quartz we have a variation of about 15 per cent. over the same range, and a variation of about 10 per cent. in the range 5890 to 2570.

For the purposes of the work now to be described, the lens acted very well. A clear, sharp image could be formed on the slit of the spectrograph, and the photograph obtained showed a linear spectrum extending from the visible to the ultra-violet, with very fair definition over the whole range. The focal length of this lens was about 70 cm.

For the dispersion at the red potassium lines, a single flint-glass prism and an ordinary laboratory spectroscope was used, the telescope being replaced by a camera for photographic purposes. Photographs in the red were difficult to obtain, because of the small intensity of light obtainable with a small collimator, and also, of course, because of the insensitiveness of photographic plates in this region. Wratten and Wainwright's spectrum plates were used, and, after some experience of the behaviour of the vapour, some satisfactory photographs were obtained. The photographs reproduced in Plate 2, fig. 1, show the dispersion curves in the neighbourhood of the two red potassium lines at 7699 and 7665. The series of photographs correspond to vapours of increasing density, and so greater dispersion. In the first three the region of the spectrum between the two lines is clearly visible, being drawn out into a fine line, nearly perpendicular to the direction of the normal spectrum. In the last photograph the dispersion is much greater; the slit of the spectrograph was widened, and the region between the lines has disappeared. This, no doubt, is partly due to absorption, but also to the fact that the dispersion is so large that the actual intensity is very much diminished at any one place. These curves are very beautiful when seen through the telescope of the spectroscope, and the gradual increase of dispersion can be watched from the time the tube is heated. As the dispersion is increased, absorption also increases, spreading chiefly from the yellow and the red at the extreme end of the visible spectrum inwards towards the two red lines. The two actual absorption lines at 7699 and 7665 also broaden, but not so rapidly as the absorption regions in the orange and extreme red, so that the part of the spectrum seen in this region, when the vapour gets dense enough to cut off nearly all the light, is two red portions of the dispersion curve on opposite sides of the potassium lines, and deviated on opposite sides of the position of the undeviated spectrum. With denser vapour still, the curve on the red

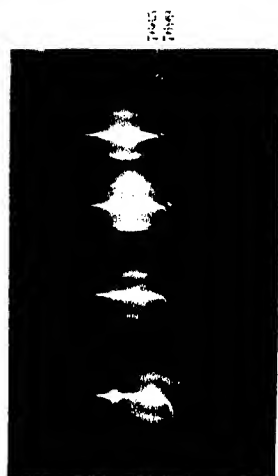


FIG. 1.

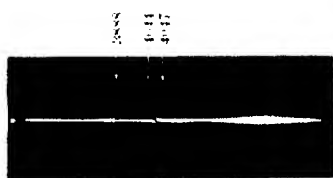


FIG. 3.

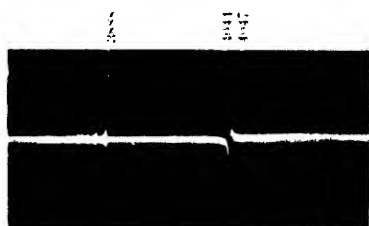


FIG. 4.

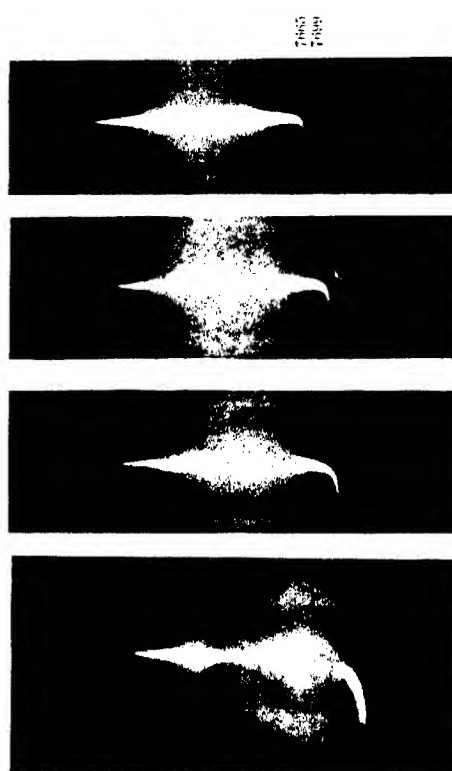


FIG. 2.



FIG. 5.



FIG. 6.

side disappears, and we get a short piece of the red on the orange side of the lines deviated a considerable distance from its original position. These effects have not been photographed with success, as the intensity of the light becomes too little, and the conditions cannot be kept steady enough for an exposure of some hours, which would be necessary. The shape of dispersion curves does not seem to be affected by the absorption regions in the orange-red and the extreme red. The curves observed seem to keep their character, and only lose the intensity of the light. This fact points to a difference of mechanism in the vibrating systems corresponding to the lines in the region of which dispersion takes place and those regions where absorption takes place without appreciable deviation, except that corresponding to the lines of the other type. These absorption regions are seen to consist of a very large number of fine lines, if sufficient resolving power be used, as has been shown by Carter, who has pointed out that the orange-red absorption region for potassium is very similar to the corresponding region investigated by Wood for sodium.*

When a very considerable amount of dispersion appears at the red rays, the dispersion begins to show itself at the violet rays 4047, 4044. It is difficult to follow the effects near these lines visually, as they are near the end of the visible spectrum, but similar phenomena can be observed, and it is easier to obtain photographs showing similar curves to those at the red pair. For the region round these lines, and also about other lines of the principal series in the ultra-violet, the quartz spectrograph used for work described in a former paper communicated to the Royal Society was employed,† and I take this opportunity of again thanking the Government Grant Committee for enabling me to purchase this instrument. The arrangement of apparatus was practically the same as for the visible spectrum, the quartz lens already described being used. Fig. 4 shows an enlargement of the dispersion curves found in the region of the lines 4047, 4044, fig. 3, being the same photograph without enlargement. Here the region between the lines is clearly visible, though now the difference of wave-length is only 3 Ångström units. Thus, with considerable density of vapour—at this stage the red end of the spectrum has disappeared nearly down to the position of the D lines—giving a considerable deviation of light near the lines 4047, 4044, there is very little absorption in between these lines;

* 'Physical Review,' vol. 27, 1908. I was not aware of this work by Carter when I communicated a paper to the Physical Society of London on the absorption spectrum of potassium ('Phil. Mag.,' January, 1910). The similarity there discussed between the spectra of potassium and sodium had been observed and commented on by Carter before that paper was written.

† 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 421.

in other words, there is little absorption within one Ångström unit of the actual absorption lines. A similar fact was, of course, observed by Becquerel in the case of sodium, and afterwards by Wood.

At the next pair of lines of the principal series, wave-lengths 3447·49, 3446·49, anomalous dispersion also takes place, but it is of small amount, and hitherto no light has been detected between the two lines. The dispersion curves observed are then similar to those for a single line, and the same is true for higher members of the series at which the dispersion can be detected. These dispersion effects have been observed at the first seven lines of the series, or, rather, pairs of lines. Figs. 5 and 6 show the curves at the lines 4047, 3447, 3217—the effect is very small at the last of these, and smaller still at the next three lines. It is, however, certainly observable in certain negatives when examined carefully under a microscope.

Measurements have been made on the amount of the deviation, with a view to finding the relation between the constants for the Sellmeier dispersion formula which is applicable to the case. In this way there seems some hope of obtaining information as to the vibrating systems to which these lines are due, and hence as to the constitution of the atom.

We shall first consider the measurements of deviation obtained from photographs of the type of fig. 5, deferring the consideration of the more detailed measurements about the lines 7699 and 7665, and 4047, 4044. To obtain photographs of this type, dense vapour has to be used and the red end of the spectrum is completely absorbed, and also the light between 4047 and 4044 disappears. The curves obtained can then be regarded as corresponding to a set of single lines in the mean positions of actual pairs of the principal series.

The quantities to be measured were the displacements of points due to light of particular wave-lengths owing to the deviation produced by the vapour prism from their positions in the undeviated spectrum. This would be simply proportional to the deviation of the rays if the effective distance of the photographic plate from the slit of the spectrograph were the same for all colours. But with the quartz spectrograph a considerable tilt has to be given to the plate in order that various parts of the spectra should be in focus together. We therefore have the images of the slit of continuously varying length along the spectrum, increasing from the violet to the red. This change of length of the image of the slit is considerable. If the length of the image of the slit for light of wave-length 2400 be 1 that for light of wave-length 6000 is about 1·4. Measurements, therefore, of length perpendicular to the spectrum have to be corrected owing to this circumstance. The relation between the length of

image of the slit and the distance from some origin on the plate is not exactly a linear one, as the plate is bent slightly in the holder, the surface of good focus not being exactly a plane, but this made a small effect which could be neglected, and as far as the present measurements are concerned the continuous spectrum due to any point on the slit could be regarded as a straight line in the negative. This approximation was useful, as measurements of the displacement could be made from the image of a speck of dust on the slit. The actual method adopted was to rule on the negative with a needle point a fine line parallel to the image of the speck of dust and make measurements from this line. The reason for not using the dust line directly was that it was not continuous enough. Two sets of corrections were made to these observed lengths—firstly, owing to the fact that the ruled line was parallel to the dust line, and hence, owing to the tilt effect, could not be parallel to the undeviated spectrum; and secondly, owing to the tilt effect on the actual measurements. Curves of corrections were drawn from measurements on the breadth of a continuous spectrum—the dispersion increasing in the violet makes the relation between length of image of the slit and wave-length not linear—these correction curves gave a quantity to be added to and a factor to multiply each measurement of deviation. It was no use attempting to photograph the undeviated spectrum on the same plate as the deviated and measure from this directly, as the deviations measured in the smaller wave-lengths were so small that comparison of the two spectra rendered this method impossible. The actual readings were made with a micrometer microscope reading directly to 0.01 mm. Measurements on negatives of the type represented in fig. 4 could not be made with any accuracy for regions corresponding to wave-lengths greater than about 4500—the line on the red side of this position being very much broadened out and losing all sharpness. Measurements close to the positions occupied by the absorption lines at wave-lengths 3100 and 3034 are also of not much value. The lines become blurred close to the absorption region, and the measurements tabulated can only be taken to mean that the anomalous dispersion effect is really observable. Anomalous dispersion could be observed at the next line, 2992, but no quantitative estimate could be made. The measurements finally corrected were not from the undeviated line, but from an arbitrary base line. The position of the undeviated line was first obtained roughly from the negative, and then a corrected value found for its position relatively to the arbitrary line by taking an arbitrary set of points and applying the dispersion formula to be discussed later. The positions of the undeviated spectrum determined in this way agreed to within 0.001 cm.

For measurements quite close to absorption lines a set of lines was ruled

on the negative parallel to the slit images, and the wave-lengths corresponding to these lines determined in the ordinary way. In this manner readings close to the absorption line could be obtained. At other places known lines in the arc spectrum were used, and also specially ruled lines. On the negatives used for measurement there was a sufficiency of lines extending across the spectrum, due to diffused light from the arc, to determine with sufficient accuracy the wave-length corresponding to any position on the dispersion curves. It was found that the deviations on any one negative were, at different wave-lengths, proportional to those on any other. The following table gives the deviations for the wave-lengths in the first column for the best negative:—

Wave-length.	Deviation.	Wave-length.	Deviation.
5460	0·108	3466	0·028
5135	0·085	3453	0·026
4850	0·070	3444	0·086
4593	0·060	3441	0·033
4555	0·060	3390	0·029
4390	0·055	3340	0·027
4227	0·047	3303	0·025
4128	0·041	3226	0·024
4078	0·031	3220	0·022
4064	0·021	3215	0·025
4060	0·016	3213	0·024
4055	0·001	3207	0·024
4040	0·091	3110	0·021
4033	0·067	3095	0·022
4000	0·050	3067	0·021
3969	0·046	3040	0·020
3934	0·042	3030	0·022
3884	0·041	2960	0·019
3724	0·037	2850	0·017
3616	0·035	2700	0·015
3491	0·031	2600	0·016
3476	0·029	2500	0·015

The actual measurements were made to one more decimal place than is recorded; but as the line on which the cross wire was set was not very definite, this last figure has been omitted, and the nearest number to the mean of the observed values tabulated. The error in any of the numbers is not more than 0·001 as far as observational errors are concerned.

In the curve (fig. 7) these values are plotted, and this represents the complete dispersion curve for the vapour from the region about 5000 to the ultra-violet 2400. The observed values of the deviations are represented by dots about the curve.

The deviation being equivalent to that due to a thin prism is propor-

tional to $n-1$, where n is the refractive index for light of a particular wave-length. The Sellmeier dispersion formula may be written

$$n^2 - 1 = \sum \frac{m_1 \lambda^2}{\lambda^2 - \lambda_1^2},$$

where λ is the wave-length of the light corresponding to the refractive index n , and λ_1 , etc., are the wave-lengths corresponding to absorption lines, m_1 , etc., being constants.

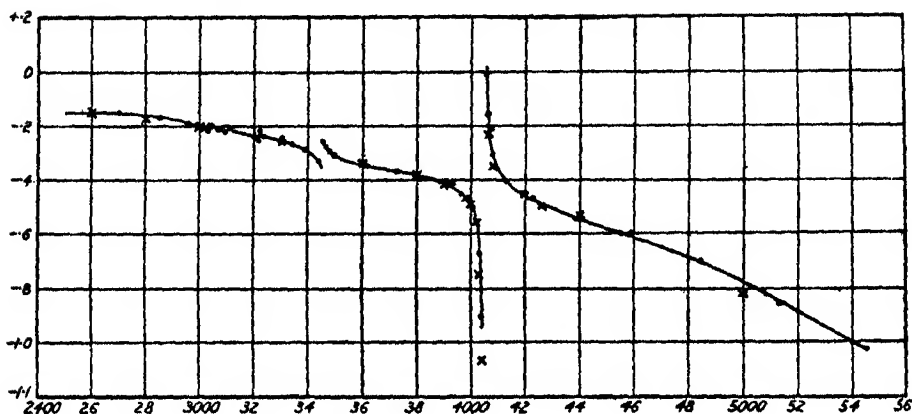


FIG. 7.—Abcissa is wave-length; ordinate is deviation.

For a first approximation for our case we can take the dispersion as that corresponding to two absorption lines at wave-lengths 7682 and 4045, corresponding to the means of the two first pairs of the principal series. It is clear from the curve of fig. 7 that the effect of the absorption lines of smaller wave-length is only noticeable in their immediate neighbourhood, so that for all except such wave-lengths the assumption of the two constants for our formula will be near enough to the actual circumstances of the case. We can afterwards obtain an estimate of the value of the constants m_3 , m_4 , corresponding to the higher lines of the series. Now as n is nearly equal to 1, $n^2 - 1$ may be taken as equal to $2(n-1)$, so that our curve should represent values proportional to

$$\frac{m_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{m_2 \lambda^2}{\lambda^2 - \lambda_2^2}, \quad (1)$$

except for values of λ quite near λ_3 and λ_4 .

We may therefore take, for applying the Sellmeier theory to our case, δ , the deviation at any wave-length λ , as equal to the expression just written down. The observed deviation was in the first instance measured from an arbitrary base line parallel to the undeviated position of the linear

spectrum. A little uncertainty remained as to the actual position of the undeviated spectrum, so that calling the observed value of the deviation measured from the roughly estimated position of the undeviated spectrum δ' we have

$$\delta' + x = \frac{m_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{m_2 \lambda^2}{\lambda^2 - \lambda_2^2},$$

when x is a small quantity to be determined which is constant for all wave-lengths.

The ratio $m_1 : m_2$ was found by taking points on the curve at which the deviations are equal. These points must, of course, be on opposite sides of the line 4045. Such a pair of points are at $\lambda = 3940$ and $\lambda = 4140$. In this way, taking several points, we obtain

$$m_2 : m_1 = 0.00140.$$

m_1 was then found from pairs of values of δ' . These gave for m_1 a mean value of 0.113, so that $m_2 = 0.000158$. We can then find x and so the corrected position of the undeviated spectrum.

With these values of the constants we obtain for δ , by substituting in (1), the following values at the specified wave-lengths:—

Wave-length.	δ .	Wave-length.	δ .	Wave-length.	δ .
5500	0.119	4060	0.023	3800	0.038
5000	0.083	4040	0.107	3600	0.034
4600	0.058	4035	0.075	3300	0.026
4400	0.054	4020	0.056	3000	0.020
4260	0.050	4000	0.050	2800	0.017
4200	0.046	3980	0.047	2600	0.015
4060	0.036	3900	0.042		

All the deviations are negative, that is, the light in the whole of the region investigated travels with a velocity greater than that in vacuo.

These points are marked on the curve of fig. 5 by small crosses. It is seen that these values for m_1 , m_2 , give very fair agreement between the observed and calculated values as long as we are not quite near the other absorption lines.

If we add the term $\frac{m_3 \lambda^2}{\lambda^2 - \lambda_3^2}$ to δ and take deviations at wave-lengths near 3447, we can obtain a value of m_3 . From the observed deviations at wave-lengths 3453, 3466, 3476, 3444, 3441, we obtain

$$m_3 \times 10^6 = 10, 11, 10, 12, 13.$$

For wave-lengths further removed from the absorption line than these we

can get no result—the observational errors are too large; m_3 then can be taken to be 11×10^{-6} .

For the next line we have two observations which just give an estimate of the value of m_4 , the constant for a fourth term in δ . These observations are at wave-lengths 3215 and 3220; they give 2×10^{-6} and 4×10^{-6} . These numbers can only be regarded as giving the order of magnitude of m_4 . For the next line we cannot even get an estimate of the magnitude of the constant.

We have then finally the values

$$\begin{aligned} m_1 &= 0.113, & m_3 &= 0.000011, \\ m_2 &= 0.000158, & m_4 &= 0.000003, \end{aligned}$$

and the complete dispersion curve represented by

$$\delta = \frac{m_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{m_2 \lambda^2}{\lambda^2 - \lambda_2^2} + \frac{m_3 \lambda^2}{\lambda^2 - \lambda_3^2} + \frac{m_4 \lambda^2}{\lambda^2 - \lambda_4^2}. \quad (2)$$

We may now return to the more detailed examination of the dispersion in the region of the red and violet lines. Fig. 1 shows a series of photographs with increasing density of vapour of the dispersion curves in the red. Fig. 2 represents enlargements of the series of fig. 1. For representing these curves by the Sellmeier formula we must now use two constants for m_1 corresponding to the two wave-lengths 7699 and 7665. Calling these λ_1' and λ_1'' and the corresponding constants m_1' , m_1'' , the approximate value of δ for this region should be

$$\frac{m_1' \lambda^2}{\lambda^2 - \lambda_1'^2} + \frac{m_1'' \lambda^2}{\lambda^2 - \lambda_1''^2}, \quad (3)$$

the terms in (2) depending on m_3 , m_4 , etc., are too small to be taken into account in this region.

We could find the ratio of $m_1':m_1''$ by finding the point at which the fine dispersion line between the two absorption lines cuts the undeviated portion of the spectrum, for at this point $\delta = 0$, so (3) gives $m_1':m_1''$ directly; but the difficulty of obtaining any one wave-length accurately from photographs in this region makes this method uncertain. It may be mentioned here that this point is invariably the same whatever be the density of the vapour, as of course follows if the Sellmeier formula represents the facts. This may easily be observed by fixing the cross wires of the telescope on this point for a low density of vapour, and then gradually heating the tube to obtain denser vapour. The dispersion curve spreads upwards and downwards, but the fine bright line between the absorption lines always passes through the same point on the undeviated position of the spectrum.

The curve of fig. 8 represents the dispersion in the neighbourhood of the red lines. It was obtained from a series of four photographs of the same kind as those of fig. 1. With the photograph of the dispersed linear spectrum was photographed the spectrum from a neon tube, and also the two potassium lines (absorption) at 7699 and 7666. The neon tube, in addition to the neon lines, showed some helium lines, of which 6678, 7065, and 7282 proved useful in constructing a curve of wave-lengths. The instrument used was a simple spectrometer, with a flint-glass prism, so that

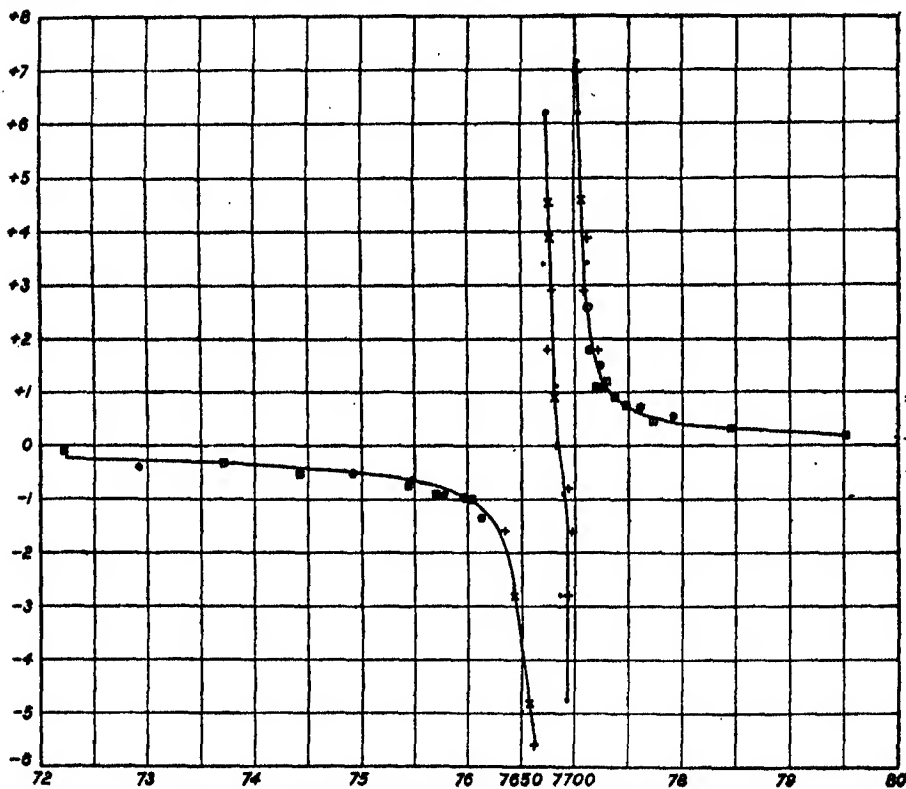


FIG. 8.—Abcissa is wave-length; ordinate is deviation.

the dispersion was small, and no great accuracy could be obtained in the measurements. The actual measurements on a single photograph were obtained by ruling fine lines parallel to the undeviated spectrum, and then finding the wave-length corresponding to the point at which the ruled line cut the dispersion curve. The deviations were thus fixed, and the wave-lengths corresponding to these were determined. The four photographs can be regarded as representations of the dispersion curve on different scales—the photograph corresponding to less dense vapour is, of course, on a smaller

scale than those corresponding to denser vapour, but it shows the dispersed light nearer to the absorption lines. By drawing curves for each photograph, the relation of scale for the series can be found, and thus a factor obtained for each to reduce all to the same scale.

The factors were 25, 8·3, 3·5, 1, that is, the measured deviations in the photograph with least dispersion were to be multiplied by 25, and so on, to bring all to the same scale as the one with greatest dispersion. These factors were determined from several points on parts of the curves represented on two photographs, and the numbers obtained agreed as well as could be expected. For example, the six numbers for the factor to multiply deviations on the second photograph to make it comparable with the third were 3·8, 3·6, 3·7, 3·6, 3·4, 3·2, with a mean of 3·5. The curves for the first and second photographs did not agree very well in the region with shorter wave-length than 7666, but in this region, on all the photographs, there was considerable spreading of the line, so that it was difficult to estimate the exact position of the intersection of the ruled line and the deviated spectrum.

The four sets of values thus obtained are plotted in fig. 8, and the dispersion curve drawn by means of them. Certain points are not represented on the curve, as they would require the rest of the curve to be on too small a scale. The following table gives the reduced deviations corresponding to the wave-lengths in the second column. The number at the side of the wave-length refers to the number of the photograph to which it belongs in the series :—

δ .	Wave-length.	δ .	Wave-length.	δ .	Wave-length.
-0·01	(4) 7222	0·71	(1) 7676	0·46	(2) 7705
-0·04	(3) 7296	0·62	(1) 7673	0·39	(2) 7708
-0·03	(4) 7371	0·40	(2) 7677	0·34	(1) 7711
-0·05	(4) 7441	0·39	(2) 7676	0·29	(2) 7709
-0·05	(3) 7496	0·34	(1) 7673	0·26	(3) 7712
-0·07	(4) 7545	0·29	(2) 7678	0·18	(3) 7714
-0·07	(3) 7549	0·18	(2) 7676	0·18	(2) 7718
-0·08	(2) 7568	0·11	(1) 7682	0·15	(3) 7722
-0·09	(4) 7571	0·09	(2) 7681	0·12	(4) 7729
-0·09	(3) 7579	0·00	(2) 7683	0·11	(1) 7722
-0·10	(3) 7600	-0·08	(2) 7691	0·11	(3) 7728
-0·10	(4) 7604	-0·09	(1) 7690	0·11	(4) 7724
-0·14	(3) 7614	-0·16	(2) 7696	0·09	(2) 7748
-0·16	(2) 7632	-0·28	(1) 7686	0·09	(4) 7738
-0·28	(2) 7644	-0·28	(2) 7692	0·07	(2) 7760
-0·39	(2) 7653	+1·77	(1) 7699	0·07	(4) 7748
-0·48	(2) 7658	0·71	(1) 7702	0·05	(3) 7791
-0·56	(2) 7663	0·64	(2) 7703	0·05	(4) 7772
+1·77	(1) 7667	0·62	(1) 7701	0·08	(4) 7846
1·29	(1) 7672				

There is a good deal of uncertainty in the measurements of the wave-lengths, the distance apart of the two absorption lines at 7699 and 7666 being almost exactly 0.1 mm., so the determination of a particular wave-length may have a considerable error. The numbers representing the deviations were measured in centimetres and divided by 3, for convenience in plotting. They are only expressed to two decimal places, as the errors in wave-length determinations do not warrant further accuracy. The decimal point is omitted on the curve.

A similar curve is shown in fig. 9 for the dispersion in the neighbourhood of the lines at 4047, 4044. This curve is from a single photograph; a

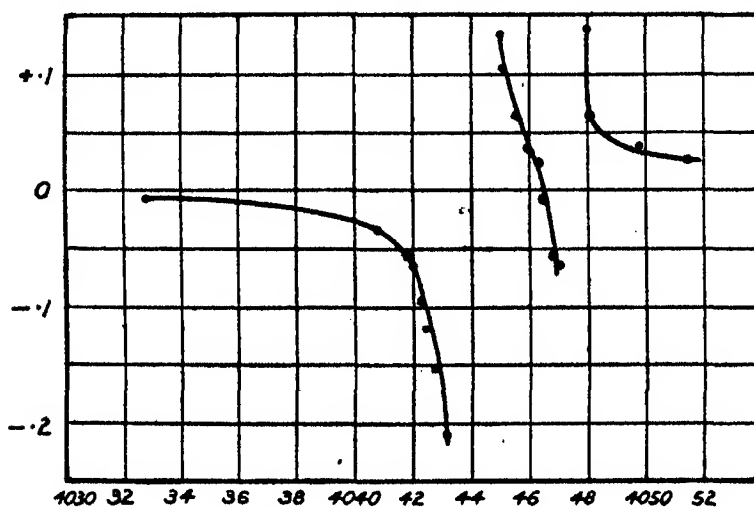


FIG. 9.—Abcissa is wave-length; ordinate is deviation.

composite curve was not constructed, as in this case the two absorption lines are so close together that the instrumental appliances would not admit of sufficient accuracy in the wave-length determinations to combine various curves. The deviations shown in this curve are not measured from the undeviated position, but they represent the deviation due to the two lines 4047, 4044. In other words, they represent the quantity

$$\frac{m_2'\lambda^2}{\lambda^2 - \lambda_2'^2} + \frac{m_2''\lambda^2}{\lambda^2 - \lambda_2''^2},$$

λ_2' and λ_2'' standing for 4047 and 4044, and m_2' , m_2'' for the quantities corresponding to m_1' , m_1'' .

The observations for the two curves representing the dispersion in the region of the red and violet lines are not accurate enough to calculate with any certainty the constants for the appropriate Sellmeier expressions.

There appears to be an equality, indicated in the ratios $m_1':m_1''$ and $m_2':m_2''$, but at present the uncertainty in the numbers makes this not very definite. The curves are of the type represented by the equation, but as a slight change in wave-length affecting all the observations would make a considerable change in the constants, I have decided to leave for the present the further investigation of these curves until measurements under greater dispersion can be obtained. There is a good deal of interest in the ratios $m':m''$, and I hope to be able to obtain more reliable curves and similar ones for other metals of the alkali group, so as to make a comparative study of the lines and the dispersion in their region for the whole group of metals. At present, the interest lies in the conclusions we can draw from the general dispersion curve.

On Drude's representation of dispersion, if we assume that the vibrating systems, which give the natural periods of the vapour, are simple negative electrons vibrating about an equilibrium position, the quantities m of the general dispersion expression will be proportional to $n\lambda^2$ when n is the number of electrons per cubic centimetre of the type giving rise to light of wave-length λ . If we suppose each molecule of the vapour to be capable of absorbing or emitting light of wave-length λ , then the number of special corpuscles per molecule is proportional to m/λ^2 . This requires far too many electrons per molecule, and we are driven to the conclusion that it is not every molecule which takes part in the absorption of light in the same way. This is on the assumption that the electrons are vibrating about equilibrium positions, but it is clear that if the vibrations are about a steady state of motion, a similar conclusion will follow. The quantities m will depend on the number of electrons which can have a certain definite oscillation about the steady state, and the enormously greater value of m for the first pair of the principal series lines and its rapidly diminishing value through the series show that it is impossible that in each molecule of the vapour there can be sufficient electrons to provide all the natural periods.

We can obtain an estimate of the number per molecule on Drude's theory for the case of sodium, for which Wood has determined absolute values of the refractive indices at a definite temperature of the vapour by an interferometer method. We do not know the actual density of the vapour at this temperature, but we can obtain an estimate of it. Jewett* has measured the vapour pressure of sodium for temperatures up to 420° C. The boiling point of sodium is estimated to be 800° C., so that by a very rough interpolation we find the vapour density to be 7.5×10^{-6} at Wood's temperature, 644° C. With this value and the value of m , as determined by Wood, 0.000055, we find on

* 'Phil. Mag.,' 1902, vol. 4, p. 546.

Drude's theory* that the number of electrons per molecule is 0.08. This, of course, gives us only the order of the number, as the numbers we have used are really only guesses, and as we have assumed that the atom of sodium is identical with the molecule. However, the number per molecule corresponding to the D absorption line is at any rate small. A similar state of things may be expected with potassium, so that with our ratio $m_1/m_2 = 700$ roughly, only about 1 molecule in about 2000 can be in operation in producing absorption at the lines 4047, 4044. Fewer still will be taking part in the absorption of lines lower down in the series; and although it appears that the ratio of successive m 's diminishes, still very few molecules, comparatively, can be taking part in the absorption corresponding to numbers near the limit of the series. We are thus led to look for the explanation of the natural periods corresponding to the series lines, not to the atom itself, but to the atom as differentiated possibly for each period of the series. The identity of structure of the atom must on this view be given up, as far, at any rate, as its properties as regards light are concerned. A suggestion of Sir J. J. Thomson† is interesting in this connection. He has put forward the view that lines in the spectrum of an element which show the Zeeman effect are due not to vibrations of corpuscles in the normal atom, but to vibrations of corpuscles which form semi-permanent combinations with the normal atom. He regards these corpuscles as forming swarms round the atom when the element is emitting light in an arc or in a flame, and so providing plenty of opportunity for temporary combinations with the normal atom. It is clear that there could be many types of temporary combination, and thus in a metallic vapour we could have normal atoms with varying numbers and arrangements of corpuscles attached to them. It will be to these arrangements, which will occur with relatively only a few of the atoms, that we may have to look for the explanation of the lines in spectra. Another view that leads to somewhat similar conclusions is that of Wood, who supposes that the principal series lines are due to atoms differing in that they have lost different numbers of negative electrons. The argument for this is that there seems to be independence between the principal series lines of sodium in the phenomena of

* On Drude's theory the constant m of the Sellmeier formula is $= N\delta$, where N is the number of electrons per unit volume giving rise to a particular period and δ is a constant connected with the wave-length and constants of the electron by the relation $\delta/\lambda^2 = e^2/\pi m$. We hence obtain, since e , m , λ are known—assuming that a negative corpuscle gives rise to the vibration— N , the number of corpuscles per unit volume. This is, for the case of sodium and the D lines, 1.6×10^{17} . The number of atoms of sodium per unit volume in the vapour at the temperature at which Wood's determination was made is 2×10^{14} approximately. Hence we would have about twelve atoms to one electron emitting the D line.

† 'Phil. Mag.' 1906, vol. 11, p. 774.

fluorescence. It is difficult on this view to see how an atom could lose sufficient corpuscles to provide enough different systems for all the lines of a series. But in any case it appears that all the atoms cannot be in operation, and that we have a real difference of physical properties indicated. One would expect that on either of these views an increase in the ionisation of the vapour would produce an effect on the number of atoms exercising a particular type of absorption, and so an effect on the dispersion of the vapour. But in any case, in the vapour of these metals there is a large amount of ionisation, and the increase due to, say, ultra-violet light may not be sufficient to produce any observable effect. I have tried the effect of cutting off most ultra-violet light from the vapour by a glass plate interposed in the path of the train of light passing through the absorption tube, and no visible effect could be observed in the dispersion in the visible part of the spectrum.

This view that the lines, at any rate of the principal series, in spectra are due to special atoms simplifies the picture we must make of the atom itself. We no longer need to provide such an enormous number of degrees of freedom for each individual atom, and we may be able in this way to simplify some of the difficulties in the theory of the partition of energy.

On the Scattering of Homogeneous β -Rays and the Number of Electrons in the Atom.

By J. A. CROWTHER, M.A., Fellow of St. John's College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received June 18,—Read June 30, 1910.)

Introduction.

The subject of the transmission of β -rays through matter has, from time to time, received considerable attention. Apart from any intrinsic interest the problems involved are of considerable theoretical importance. Owing to the high velocity of the β -rays, the collisions, to which the absorption of the rays must be ascribed, take place not with the atom as a whole, but with its constituent parts, and thus from a study of the behaviour of the rays during their passage through matter we may hope to gain considerable information as to the constitution of the atom.

Until very recently it was thought that the phenomena involved in the absorption of the β -rays were very simple. It was early shown that the β -rays from a single radioactive substance, such as uranium X for example, were absorbed by light substances, such as aluminium, according to an exponential law. For the heavier elements, such as tin or platinum, the absorption curve at first descended rather more steeply than the true exponential, but finally became exponential after the rays had passed through some small thickness of the absorbing material. This law has been tested for a large number of elements and compounds by the present writer,* and with a high degree of accuracy, for a few substances, by N. R. Campbell.†

This being so, the fact that a given bundle of rays was absorbed according to an exponential law was regarded as proving that the rays were homogeneous, and, further, that their velocity did not appreciably alter during their passage through the absorbing material. Quite recently, however, W. Wilson‡ published results which threw some doubt on both these conclusions. Instead of working with the β -rays from a single radioactive substance, he used the mixed bundle of rays from radium, employing a magnetic field to sort them into a series of nearly homogeneous pencils. He then found that the absorption of the "homogeneous" rays thus obtained did not follow an exponential law, but that it could best be represented by

* J. A. Crowther, 'Phil. Mag.,' 1906, vol. 12, p. 379.

† N. R. Campbell, 'Phil. Mag.,' 1909, vol. 17, p. 180.

‡ W. Wilson, 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 612.

a linear relation. As we shall see later, this linear relationship is not strictly true, the absorption curve for a substance such as aluminium having in reality two points of inflection. We shall return to this point later.

In the same paper Wilson also gave results suggesting that the β -rays lose velocity in their passage through the absorbing medium. This point has been since investigated by the present writer,* who found, by direct measurements of the velocity of the rays before and after transmission through absorbing sheets, that a small but distinct loss of velocity did occur, and similar results have been recorded still more recently by Wilson† himself.

In a previous paper‡ I have shown that the absorption of a parallel pencil of β -rays may conveniently be divided into two stages: firstly, the scattering or diffusion of the pencil, and, secondly, the more gradual absorption of the diffuse rays. Without considering for the moment whether the two phenomena are really distinct, or whether they may not be merely two different expressions of the same phenomenon, we may regard it as an experimental fact that a parallel pencil of β -rays is considerably scattered in a thickness of material too small to produce any appreciable absorption in a uniformly diffused beam. It will be convenient, therefore, to consider the two phenomena separately.

Moreover, as now appears, the measurement of the absorption of the rays, as made by ionisation methods, is open to some uncertainty. In all ionisation methods it is assumed that the amount of ionisation produced is a simple measure of the intensity of the rays producing it. So long as the velocity of the rays remains the same, this is in all probability accurately the case. When, however, the velocity is changing, as appears to be the case to some extent during the absorption of homogeneous β -rays, the assumption is no longer so obvious, and it is uncertain whether the ionisation produced measures the energy of the rays, their number, or some function of the two; while if secondary radiation is at all important it may also depend upon the substance and shape of the ionisation chamber.

Measurements on the scattering of a pencil of β -rays do not suffer from these uncertainties. As pointed out above, the rays are scattered in a thickness of material far too small to produce any appreciable effect on the velocity of the rays, and possible errors due to this cause are therefore eliminated. For this reason experiments on the scattering of the β -rays are

* J. A. Crowther, 'Camb. Phil. Soc. Proc.,' 1910, vol. 15, pt. 5, p. 442.

† W. Wilson, 'Roy. Soc. Proc.,' June, 1910.

‡ J. A. Crowther, 'Roy. Soc. Proc.,' 1908, A, vol. 80, p. 186.

far more suitable for the investigation of the constitution of the atom than the more complex phenomena of absorption.

Theory of the Scattering.

Prof. Sir J. J. Thomson* has very recently published a theoretical solution of the problem of the scattering of rapidly moving electrified particles. For the complete investigation the original memoir should be consulted. We shall, however, abstract here as much as will be necessary for the purposes of the present paper.

When a β -particle passes through an atom of a substance it will be deflected. The amount of this deflection will, of course, depend upon the way the particle strikes the atom. There will, however, be a mean value for this deflection, and, considering only the effects produced by large numbers of the β -particles, it may be assumed that each particle suffers the mean deflection. Since the direction of the deflection is arbitrary, the problem is the same as that of finding the average value of the resultant of n displacements of arbitrary phase and of constant amplitude θ . This value is known to be $\sqrt{n}\theta$. Thus if N is the number of atoms per unit volume, b is the radius of an atom, and θ the mean deflection of a β -particle produced by an atom, then the mean value of the deflection experienced by a particle in passing through a plate of thickness t is $\sqrt{(N\pi b^2 t)}\theta$. Calling this angle ϕ_m , we have for any given substance

$$\phi_m/\sqrt{t} = \text{constant.}$$

If ϕ is a given angle, the probability that the deflection is greater than ϕ is equal to $e^{-\phi^2/n\theta^2}$ or $e^{-\phi^2/ct^2}$, where c is a constant, since n varies directly as the thickness t . Thus, if t_m is the thickness for which this probability is one-half, we have

$$e^{-\phi^2/ct_m^2} = \frac{1}{2}, \quad (a)$$

or

$$\phi/\sqrt{t_m} = \theta\sqrt{(c \log_e 2)}, \quad (1)$$

which is constant for any given absorbing substance.

The probability that the deflection is less than ϕ is equal to $(1 - e^{-\phi^2/ct^2})$, that is to

$$1 - e^{-k/t} \quad (2)$$

where k is a constant for any given value of ϕ .

Both these relationships lend themselves readily to experimental verification.

To calculate the value of θ , the atom is regarded as consisting of N_0

* Prof. Sir J. J. Thomson, 'Camb. Phil. Soc. Proc.,' 1910, vol. 15, Pt. 5.

negative corpuscles accompanied by an equal quantity of positive electrification. The deflection of the β -particle will thus arise from two causes:—

(1) The repulsion of the negative corpuscles distributed through the atom; and

(2) The attraction of the positive electrification.

The deflection due to the latter will depend upon whether the positive electricity is uniformly distributed through the atom, or whether it is divided up into small units. Prof. Thomson considers each of these suppositions separately. It will be sufficient here to give the results which he arrives at. He found that the mean deflection ϕ_m produced by passage through a thin plate of thickness t was given by

$$\phi_m = \frac{e^2}{m\epsilon^2} \left\{ \frac{384}{25} N_0 + \frac{\pi^2}{16} N_0^2 \right\}^{\frac{1}{2}} \sqrt{N\pi t} \quad (\text{A})$$

if the positive electricity is uniformly distributed; and by

$$\phi_m = \frac{e^2}{mv^2} \left[\frac{384}{25} N_0 \left\{ 2 - \left(1 - \frac{\pi}{8} \right) \sigma^{\frac{1}{2}} \right\} \right]^{\frac{1}{2}} \sqrt{N\pi t} \quad (\text{B})$$

if the positive electricity is in small separate units; σ being here the ratio of the volume occupied by the positive electricity to the volume of the atom.

The main object of the present experiments has been to test as completely as possible the agreement of the above relationships with the experimental facts, and, if the agreement proved to be satisfactory, to determine the value of N_0 , the number of corpuscles in an atom, for a number of different elements.

Experimental Details.

Before proceeding to describe the results obtained, it will be necessary first to give a brief account of the experimental methods employed.

The source of the β -radiation was a sample of about 30 milligrams of radium bromide, in radioactive equilibrium, enclosed in a small glass tube. This was found to give out β -rays having a continuous range of velocities from about 2.35×10^{10} to 2.92×10^{10} cm. per second. These were sorted into bundles of rays having nearly the same velocity by a magnetic field.

It may be permissible here to point out the limitations of the magnetic deflection method, especially as they do not seem to have been quite grasped by some previous users of the method. Various screens are arranged, as in fig. 1, to mark out a circular path ACB, and a magnetic field is applied at right angles to the plane of the paper. By suitably adjusting the strength of this field, rays entering the system at A can be made to trace out the path ACB and emerge through B into a suitable measuring vessel. If, however, the apertures have a finite size, as must always be the case in practice,

the path ACB is not the only possible path for rays to follow in order to get through the aperture B. A little consideration will show that rays of uniform velocity, if entering the field obliquely, may be transmitted through the system along paths such as acb or $a'c'b'$, even when the field is too strong or too weak to deflect the normal rays along the path ACB. In this way, even if the rays are uniform to begin with, there will be a definite range of field strength for which some of the rays can pass through the system. Conversely, if the rays are not homogeneous to begin with—if, for example, we are dealing with the whole of the β -rays from radium—there will be for every magnetic field a finite range of velocities which the β -rays may possess and still be able to pass through the system. Unless the size of the apertures employed is quite small compared with the radius of the path, this range of velocities will be very considerable, and the emergent beam

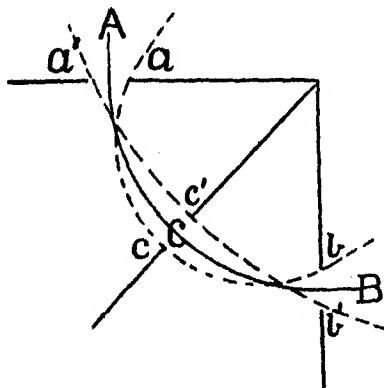


FIG. 1.

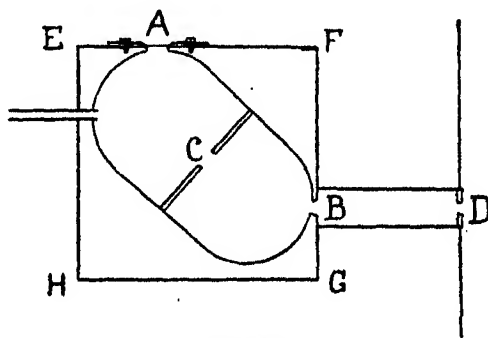


FIG. 2.

far from homogeneous. It is important, therefore, that the apertures be kept as small as possible. On the other hand, as the quantity of β -rays which can be radiated through a given area by any radioactive substance is limited, the size of the apertures is ultimately fixed by the sensitiveness of the measuring arrangements.

One further point of importance remains to be noticed, namely, the possible scattering of the rays during their passage through the air. Some preliminary experiments* which were undertaken to test this matter showed that if the path of the rays was at all long, say, even 4 or 5 cm., the scattering of the rays by the air was very considerable. In order to ensure the homogeneity of the transmitted rays, and still more in order to obtain a parallel pencil such as was required for the present experiments, it was necessary to

* J. A. Crowther, 'Camb. Phil. Soc. Proc.', 1909, vol. 15, pt. 3, p. 273.

perform the whole operation of deflecting the rays, and forming them into a suitable pencil, *in vacuo*.

The form of apparatus finally decided upon is shown in section in fig. 2. The portion EFGH is placed between the poles of an electromagnet, so that the edges of the pole pieces lie along EF and FG. The tube BD projects from the magnetic field and is screened from it as carefully as possible by a thick block of soft iron. The radius of curvature of the path of the rays is 4 cm., the diameter of the apertures at A and C is 0.5 cm., and the diameter of those at B and D 0.3 cm. The depth of the box at right angles to the plane of the paper is 1.8 cm. The different apertures are bevelled and the screens and sides of the box lined with aluminium to avoid as far as possible any secondary radiation. The radium was placed immediately above A, and the aperture at A was closed with thin aluminium foil (0.002 cm.), while the tube D was soldered into the scattering chamber. The whole could be exhausted through the tube *t*, which was connected to a pressure gauge and pump.

With this apparatus a very satisfactory pencil of homogeneous β -rays was produced. By constructing a pair of such chambers and using the second to measure the velocity of the rays transmitted through the first, it was found that the extreme velocities of the β -rays passing through either of the systems did not differ by as much as 1 per cent. from the mean. The greatest possible deviation from the normal of the rays passing through D was less than 5° .

The emergent pencil of rays after leaving D entered the exhausted chamber S (fig. 3). By means of a rotating sector P, which could be operated from without, the rays could be allowed to go straight on, in which case the whole of the pencil passed into the ionisation chamber, or made to pass through different absorbing screens mounted upon the sector. The opposite face of the chamber S was closed with a thin aluminium window 6 cm. in diameter, but stops of varying aperture could be inserted in the window at R, to limit the emergent beam to any desired angle.

The ionisation chamber T calls for little comment. The face towards the chamber S was closed with aluminium leaf, and an aluminium leaf mounted on a wire ring also formed the inner electrode *e*. The other face was hollowed out, so that at whatever angle the rays emerged from the screens at P they should all have the same length of path in the ionisation chamber itself. In this way any correction for the increased ionisation due to the increasing length of path of the more oblique rays was rendered unnecessary.

The inner electrode *e* was connected by a wire passing through an earthed

tube to the key K and the inclined electroscope W. On account of the large ionisation produced in the neighbourhood of the apparatus by the γ -rays from the radium, the connecting tubes, etc., were filled with sulphur, and where this was impossible, as in the key, the actual air space was kept as small as possible.

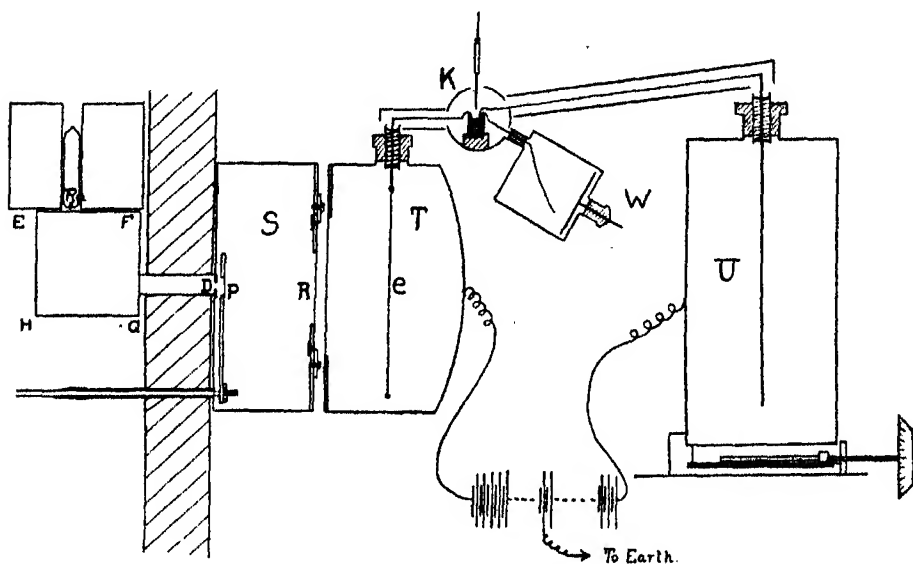


FIG. 3.

The actual measurements were made by a compensating method, the uranium shutter compensator devised for the measurement of the scattering of the uranium rays being again employed. As this apparatus is fully described in a previous paper,* it will not be necessary to give the details here. In brief the method consists in attaching to the same electroscope as the ionisation chamber S a second ionisation chamber U charged to the opposite potential. The ionisation in the latter can be varied in a known manner by means of a shutter sliding over a surface of uranium oxide. The shutter is moved in or out until a balance is obtained between the two ionisation currents, when the ionisation can be obtained from the reading of the shutter.

This method has two special advantages in the present experiments. As a little consideration will show, the processes employed to obtain a satisfactory pencil of homogeneous rays cut down the β -radiation which eventually reaches the ionisation chamber T to a very minute fraction of its original

* J. A. Crowther, 'Roy. Soc. Proc.,' 1908, A, vol. 80, p. 186.

amount. The γ -rays, on the other hand, though shielded off as far as possible by 4 cm. of lead and 3 cm. of iron, still produced a very considerable ionisation in the chamber T. If a direct timing method had been employed, the ionisation due to the β -rays would have come out as a relatively small difference between two large ionisation currents. As the percentage accuracy with which an ionisation current can be measured does not increase (beyond a certain point) with the magnitude of the current, this difference could not have been measured with any degree of accuracy. With the compensating method, however, the ionisation due to the γ -rays can be compensated to begin with, and the actual ionisation due to the β -rays themselves can be measured with precisely the same degree of accuracy as if the γ -ray ionisation were not present.

The second advantage is that the results are not affected by defects in the insulation, as would be the case if a timing method were employed. As defective insulation only comes into play when the gold leaf system has actually acquired a charge, it cannot affect the direction in which the leaf would begin to move, and hence cannot affect the final balance. In a timing method of measurement defects in the insulation will alter the rate of movement of the leaf, and may cause considerable errors in the results. This is of importance in the present case, as it is always difficult to secure a high degree of insulation in the presence of any considerable amount of radium.

A few words may be added to indicate the order of accuracy to be expected in the measurements. The maximum ionisation I_0 due to the β -radiation amounted to about 30 on the compensator scale, and it was possible to balance to within 0.5 of a division. The readings could therefore be made to an order of accuracy of about 2 per cent. of the maximum ionisation. After the rays had been cut down to one half (as in the measurement of t_m , the thickness required to produce this effect), readings could therefore be made to an accuracy of about 4 per cent., and results obtained on different occasions were generally found to agree to within about this amount. The probable error in the ionisation measurements may therefore be regarded as being about 4 or 5 per cent.

The angle of emergence of the rays was obtained by measuring the diameter of the stop and the fixed distance of the stop from the scattering layer; these could readily be ascertained to 1 per cent. The thickness of the scattering layers was measured by finding the weight of sheets of known area. This operation could also be readily performed to an accuracy of 1 per cent. If, however, the sheet used was not of uniform thickness, an error might be introduced from the fact that the rays actually passed

through only a small part of the area. Any error due to this cause can be eliminated by taking a number of readings, using different portions of the sheet, and any serious departure from uniformity was only to be expected in the case of very thin leaf.

Experimental Results.

The theory which has been described in the previous pages lends itself to experimental tests in three different ways.

(i) If the stop at R remains the same, so that the angle ϕ over which the rays can emerge into the ionisation chamber remains constant while the thickness t of the absorbing screen is varied, we have from equation (2)

$$I/I_0 = 1 - e^{-k/t},$$

where k is a constant when ϕ is constant. This may be conveniently tested in the form

$$t \log_e (1 - I/I_0) = \text{constant.} \quad (3)$$

(ii) If t_m is the thickness of material required to cut down the radiation through a given stop of angle ϕ to one half its original value, we have, from equation (1),

$$\phi / \sqrt{t_m} = \text{constant.} \quad (4)$$

(iii) From either of the equations (A) and (B) we have

$$\frac{\phi}{\sqrt{t_m}} \propto \frac{1}{mv^2}$$

when the absorbing medium remains the same and the velocity of the incident rays is varied. Keeping the same stop, and therefore keeping ϕ constant, we have

$$mv^2 / \sqrt{t_m} = \text{constant.} \quad (5)$$

Using aluminium as the absorbing medium, a series of experiments were made to test all these relationships. A considerable number of experiments were also made, using platinum as the absorbing substance, this element having been selected as being as unlike aluminium, both in density, atomic weight, and the possibility of a secondary radiation, as possible. In the case of every substance employed, sufficient readings were made to show that the relationship (4), which is the real criterion of the applicability of the theory, was valid. The results obtained are contained in the following tables.

Table I is a specimen set of readings for aluminium, obtained by keeping the stop which limits the angle of emergence of the rays fixed, and interposing varying thicknesses of aluminium in the path of the rays. I_0 is the intensity of the incident beam; I the intensity of the rays getting through the stop after passing through a thickness t of aluminium. Thus I/I_0

measures the proportion of the β -rays which have their path deflected through an angle less than ϕ in a thickness of aluminium t . The values of I/I_0 plotted against the corresponding thickness t are given in fig. 4.

Table I.—Aluminium.

$$\phi = 18^\circ. \quad v = 2.64 \times 10^{10} \text{ cm./sec.}$$

t .	I/I_0 .	$1-I/I_0$.	$\log_e (1-I/I_0)$.	$t \log_e (1-I/I_0)$.
cms.				
0.00069	0.98	0.02	-3.9	-0.0027
0.00117	0.92	0.08	-2.5	-0.0029
0.00226	0.72	0.28	-1.27	-0.0028
0.00450	0.48	0.52	-0.64	-0.0029
0.00675	0.36	0.64	-0.43	-0.0029

Hence $(1-I/I_0)$ is the proportion of the rays which have their path deflected through an angle greater than ϕ . As shown above (equation 3), $t \log_e (1-I/I_0)$ should be a constant for a given angle ϕ .

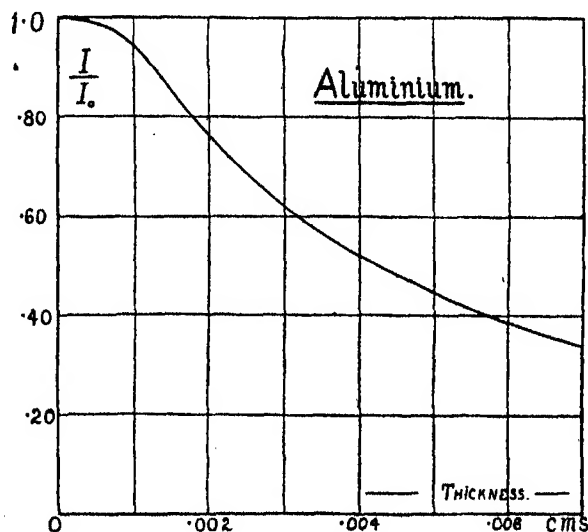


FIG. 4.

The last column of Table I gives the values of this quantity for an angular aperture $\phi = 18^\circ$, for varying thicknesses of aluminium. It will be seen that the numbers obtained are constant to well within the probable errors of the experiment. Similar experiments were made with other stops, and also with platinum as the absorbing substance. As the results were precisely similar, it will not be necessary to reproduce them at length.

Table II.—Aluminium.

$$v = 2.681 \times 10^{10} \text{ cm./sec.}$$

ϕ (radians).	t_m (cms.).	$\phi/\sqrt{t_m}$.
0.20	0.0022	4.8
0.24	0.0033	4.2
0.31	0.0054	4.2
0.41	0.0090	4.8
1.20	0.070	4.5

Table II gives the thickness t_m of aluminium which is necessary to reduce the β -radiation through a given stop of angular aperture ϕ to one-half its original value. The last column gives the values of $\phi/\sqrt{t_m}$, which according to the theory should be constant. The first four readings were obtained with the apparatus described above. The last comes from some experiments to be described later on the absorption of the β -rays, and is placed here for purposes of comparison. It will be seen that the theory is again borne out by the experimental results.

Table III.—Aluminium.

$$\phi = 18^\circ.$$

HR.	v .	mv^2/e .	t_m (cms.).	$mv^2/e \sqrt{t_m}$.
2260	2.40×10^{10}	5.41×10^{13}	0.00183	1.26×10^{15}
2870	2.58×10^{10}	7.40×10^{13}	0.00406	1.16×10^{15}
3420	2.68×10^{10}	9.15×10^{13}	0.0056	1.23×10^{15}
4050	2.77×10^{10}	11.2×10^{13}	0.0084	1.22×10^{15}
4840	2.83×10^{10}	13.7×10^{13}	0.0122	1.25×10^{15}
6500	2.90×10^{10}	18.9×10^{13}	0.0226	1.26×10^{15}

Table IV.—Platinum.

$$v = 2.68 \times 10^{10} \text{ cm./sec.}$$

ϕ (radians).	t_m (cms.).	$\phi/\sqrt{t_m}$.
0.24	0.000070	29
0.32	0.00014	27
0.41	0.00019	29
1.20	0.00193	27

Table IV gives the results of similar experiments with platinum. The agreement here is also satisfactory, though hardly so good as for aluminium. There is, however, in the case of platinum a source of error which does not occur in the case of aluminium. As will be seen from the table, it is necessary to use very thin leaf for the experiments on the scattering of the rays by platinum. The thickness of this can only be ascertained by weighing a known and considerable area of it. This gives the mean thickness of the leaf, but in leaf of this sort variations in thickness may occur from point to point; and thus it is quite possible that in any particular experiment the thickness of the small area (about $\frac{1}{16}$ th square centimetre) actually traversed by the rays departed from the mean thickness given in Column 2.

Table III deals with the question of the variation in the magnitude of the scattering with the velocity of the rays. In performing the experiments the stop was kept the same throughout, and the thickness of aluminium required to cut down the radiation through the given stop to one-half was measured for different magnetic fields. The first column of Table III gives the product of the magnitude of the field into the radius of curvature of the path. We have then

$$HR = \frac{m}{e} v$$

where m , v , and e are the mass, velocity and charge of the β -particle. Taking account of the change in mass of the β -corpuscle with velocity we have

$$\frac{e}{m} = \frac{e}{m_0} \left\{ 1 - \frac{v^2}{V^2} \right\}^{\frac{1}{2}}$$

where V is the velocity of light. Assuming Bucherer's* value, 1.76×10^9 , for e/m_0 , these equations enable us to calculate v . The product of the first two columns is equal to mv^2/c , the values of which are given in the third column of the table. The fourth column gives the corresponding values of t_m , the thickness of aluminium necessary to cut down the radiation through the fixed aperture to one-half. According to either of the equations A or B, the quotient $mv^2/c\sqrt{t_m}$ should be constant. The values of this quantity are given in the last column of the table, and it will be seen that there is again a satisfactory agreement between the theory and the experimental results. Though the actual range of velocities is not great, yet owing to the rapid change in mass with change of velocity which occurs for these fast moving particles, the value of mv^2 , which is what we are really concerned with, increases more than threefold

* Bucherer, 'Ann. d. Phys.,' 1909, vol. 28, p. 524.

in the course of the series. This is a sufficient proportional increase to afford a reasonable test of the theory.

Having now obtained satisfactory evidence that, in the three directions where it lends itself to experimental verification, the theory of Prof. Thomson does express the experimental facts concerning the scattering of homogeneous β -rays, we may now proceed to apply it to the determination of the number of electrons contained in an atom of the various elements concerned.

On the Number of Electrons in an Atom.

We are presented in equations (A) and (B) with two different solutions of the problem, based on two different assumptions; the first, on the assumption that the positive electricity is uniformly distributed through the atom, the second, on the assumption that it is segregated into small units, comparable in size with the negative electron. Since both expressions lead to the same experimental laws, the present experiments, taken by themselves, do not enable us to decide between them. I have, therefore, calculated the value of N_0 , the number of corpuscles in the atom, from both expressions, and both values are given in Table V. We shall see, however, when we come to consider the results that, in the light of other experiments, we must regard the first hypothesis as giving the true result.

From equation (A) we have

$$\frac{\phi_m}{\sqrt{t}} = \frac{e^2}{mv^2} \left\{ \frac{384}{25} N_0 + \frac{\pi^2}{16} N_0^2 \right\}^{\frac{1}{2}} \sqrt{N\pi},$$

where ϕ_m is the average deflection produced in passing through a thickness t .

If ϕ is a given angle (fixed by the stop employed), and t_m the corresponding thickness of material required to cut down the radiation through the stop to one-half, we can easily show, from equation (a), that

$$\phi/\sqrt{t_m} = \phi_m/\sqrt{t} \times \sqrt{\log_e 2}.$$

Substituting in equation (A) we get

$$\phi/\sqrt{t_m} = \frac{e^2}{mv^2} \sqrt{\log_e 2} \left\{ \frac{384}{25} N_0 + \frac{\pi^2}{16} N_0^2 \right\}^{\frac{1}{2}} \sqrt{N\pi},$$

where N_0 is the number of corpuscles in the atom, N the number of atoms per unit volume, e the charge on the β -particle in electrostatic units.

The value assumed for e is that given by Rutherford* in his paper on the charge on the α particle, namely 4.65×10^{-10} E.S. units; and N has been calculated for each element employed from the atomic weight and the density, the mass of the hydrogen atom being taken as 1.61×10^{-24} grammes. The

* Rutherford and Geiger, 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 162.

values of $\phi/\sqrt{t_m}$ and the mass and velocity of the incident β -particles are known from the present experiments.

The value of HR for the field used in the following experiments was 3420 (Gauss centimetres), this being the field which gave the maximum β -ray effect in the ionisation chamber. The corresponding values of v and m are 2.681×10^{10} cm./sec. and 1.96×10^{-27} grammes respectively.

Substituting these values, we get from (A)

$$\phi/\sqrt{t_m} = 1.84 \times 10^{-13} \{15.3 N_0 + 0.62 N_0^2\}^{\frac{1}{2}} \sqrt{\pi N},$$

and from (B)

$$\phi/\sqrt{t_m} = 1.84 \times 10^{-13} [15.3 N_0 \{2 - (1 - \pi/8) \sigma^2\}]^{\frac{1}{2}} \sqrt{\pi N}.$$

The value of σ , the ratio of the volume of the positive electrification to the volume of the atom, on the assumption that the positive electricity is aggregated into small discrete bundles, is not known. If we assume that the bundles are similar in size to the negative electrons, σ will be negligibly small. In any case it must be less than unity. In calculating the results given in Column 5 of Table V, we have assumed that it may be neglected. If, however, it has the maximum value 1, the results in this column would merely have to be multiplied by the factor 1.43.

Table V.

Element.	Atomic weight.	$\phi/\sqrt{t_m}$.	N_0 .		N_0 /Atomic weight.	
			A.	B.	A.	B.
Carbon*	12	2.0	40	44	3.32	3.7
Aluminium	27	4.25	83	156	3.07	5.8
Copper	63.2	10.0	181	765	2.87	12.0
Silver	108	15.4	320	2080	2.96	19.2
Platinum	194	29.0	605	6500	3.12	33.5

* The values for carbon were calculated from results obtained in scattering by thin films of caoutchouc. This substance contains 90 per cent. carbon, the remaining 10 per cent. being hydrogen. It was assumed in the calculations that the number of corpuscles in an atom of hydrogen had the same ratio to the atomic weight as in the carbon atom. The weight of hydrogen present is very small and cannot seriously affect the result.

Table V contains the results obtained for five different elements. The first column contains the name of the element, the second its atomic weight, the third the observed value of the constant $\phi/\sqrt{t_m}$. In each case the value given is the mean of several concordant results, using stops of different sizes, and therefore different values of ϕ . The fourth and fifth columns give

the values of N_0 , the number of electrons in the atom, on the two different assumptions (A) and (B). Columns 6 and 7 give the ratio of the number of electrons in the atom to the atomic weight, on the two assumptions.

It will at once be noticed that the ratio of the number of electrons in the atom to the atomic weight, calculated on the hypothesis (A) that the positive electricity is distributed uniformly through the atom, is remarkably constant; while, on the other hand, the results obtained on the contrary hypothesis (B), that the positive electricity is in an electronic condition in the atom, lead to a very rapid increase in this ratio with increasing atomic weight; the ratio for platinum being nearly nine times that for carbon. This holds good whatever value is assumed for σ .

From other considerations, and in particular from a consideration of the scattering of the Röntgen rays by gases, it seems very probable that the number of corpuscles in an atom is, at any rate, very nearly proportional to the atomic weight. It has been shown* that for gases in which the homogeneous secondary Röntgen radiation is not excited, the amount of primary radiation scattered by the gas is simply proportional to the mass of gas present, and practically independent of its chemical nature. This leads us at once to the conclusion that the number of electrons present in the atom is simply proportional to the atomic weight. It is quite incompatible with such a large increase in the ratio of N_0 to the atomic weight as is given by equation (B). We must conclude, therefore, that the positive electricity in the atom is not in a state comparable to that of the electron, but that it occupies such comparatively large volumes as to be capable of being considered as uniformly distributed over the whole atom.

Taking the values of the ratio of N_0 to the atomic weight given by equation (A), therefore, we see that the mean value of this ratio is very nearly 3.0, and that, with the exception of the results for carbon, which are open to a little uncertainty, the maximum variations from this value do not amount to more than about 4 per cent. This is not greater than the possible errors of the experiment, and there is no indication of any systematic variation in the ratio either with density or with atomic weight. We conclude, therefore, that the number of electrons in an atom is equal to three times the atomic weight.

Any error in the measurement of the magnetic field would of course affect all the results to very nearly the same extent. As the velocity varies very slowly with the magnetic field, any error introduced from this cause would be proportionately equal to the error in the measurement of the field. The magnetic field was measured with a Grassot fluxmeter which had been

* J. A. Crowther, 'Phil. Mag.,' 1907, vol. 14, p. 653.

tested immediately before the experiments. The readings obtained with this instrument were very constant, and it is hardly possible that any serious error should have crept in from this source.

On the Absorption of Homogeneous β -rays.

If in our experiments we make $\phi = \pi/2$, that is to say, if we include the whole of the rays which emerge at the further side of the absorbing sheet, we return to the conditions of an absorption experiment. As the thickness t_m necessary to cut down the emergent radiation to one-half varies as the square of the emergent angle, it is evident that much greater thicknesses of material will be required for such experiments than is the case where the angle ϕ is kept small. The theory of the scattering of the rays, with which we have been dealing, only strictly applies to very thin sheets of material, and we should expect discrepancies to arise from the mere increase in the thickness of the absorbing sheet. In addition to this, we have also the complications introduced by the gradual change in velocity of the rays during their passage through such sheets. However, it was thought that experiments on the absorption of a beam of homogeneous β -rays, from this point of view, might prove interesting, and might help to elucidate the results obtained by Wilson.

The vacuum chamber S was removed, the exit tube D being closed with a thin aluminium window (0.002 cm. thick). The absorption due to this window could be obtained by extrapolation from the experimental curve. It was, however, negligible. The ionisation chamber T was replaced by one of hemispherical shape, again in order to ensure that all the rays emerging from D, at whatever angle, should have the same length of path in the ionisation chamber. By means of metal slides, sheets of absorbing substance of different thicknesses could be inserted in the path of the rays at D. The methods of measurement were otherwise the same as those described above.

Experiments were made with aluminium and platinum. The results obtained are given in Table VI, and the values of I/I_0 for aluminium are plotted against t the thickness in fig. 5. On comparing this curve with the curve for the scattering by aluminium, it will be at once perceived that both have the same general characteristics. The intensity of the transmitted radiation at first decreases very slowly as the thickness of the absorbing sheet is increased, then much more rapidly, and finally more slowly again as the curve approaches the axis of t . Owing to the small amount of radiation transmitted it was impossible to determine the exact shape of this last portion of the curve. It did not differ appreciably from an exponential curve.

Table VI.

Thickness t (cms.).	I/I_0 .	$\log_{10} I/I_0$.	$t \log_e (1 - I/I_0)$.
Aluminium.			
0.002	1.00	—	—
0.004	0.998	—	—
0.012	0.96	1.98	-0.037
0.033	0.77	1.99	-0.048
0.049	0.62	1.79	-0.046
0.073	0.29	1.46	-0.023
0.110	0.12	1.08	-0.016
Platinum.			
0.00	1.00	—	—
0.00107	0.71	1.85	-0.00134
0.00220	0.58	1.72	-0.00168
0.00327	0.38	1.58	-0.00159
0.00556	0.28	1.36	-0.00140

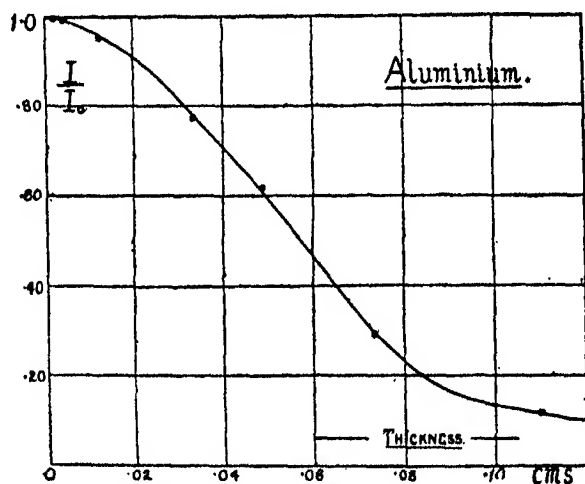


FIG. 5.

Turning again to the table, we find that the values of $t \log_e (1 - I/I_0)$ given in the last column of the table remain appreciably constant until a thickness of about 0.05 cm. is reached; after this point they begin to show a rapid decrease. Taking the first portion of the curve then, and calculating the corresponding value of $\phi/\sqrt{t_m}$ as before, we obtain the value 4.5 given below the dotted line in Table II. As will be seen from that table, this value agrees well with the values obtained from the experiments on the scattering. The first stage in the absorption of such a homogeneous pencil of rays

as we have been considering consists, therefore, in the scattering or diffusion of the beam according to the laws we have already considered.

We may now attempt to give some explanation of the "linear" law propounded by W. Wilson.* The curves given in his paper for aluminium, which is the only element for which he gives the figures, differ from the one drawn in fig. 5 principally in not showing the initial gradual decrease and the first point of inflection. In general, they do show the gradual bending round of the final portion along the axis of t , though Wilson himself seems inclined to ascribe this result to experimental imperfections. Now in Wilson's experiments the β -rays fall upon his absorbing sheets in a fairly narrow pencil; they should, therefore, exhibit the effects of scattering as described above. On the other hand, as the beam was not deflected in a vacuum, but was passing through air along its whole course, it was already partially scattered before it fell upon the absorbing sheets. Thus the portion of the scattering which corresponds to the nearly horizontal initial portion of the curve had taken place before his measurements commenced. It will be seen that the middle portion of the curve in fig. 5 is approximately a straight line.

Turning now to the case of platinum (fig. 6), the curve presents a somewhat different appearance. Here again, however, if we consider only the first

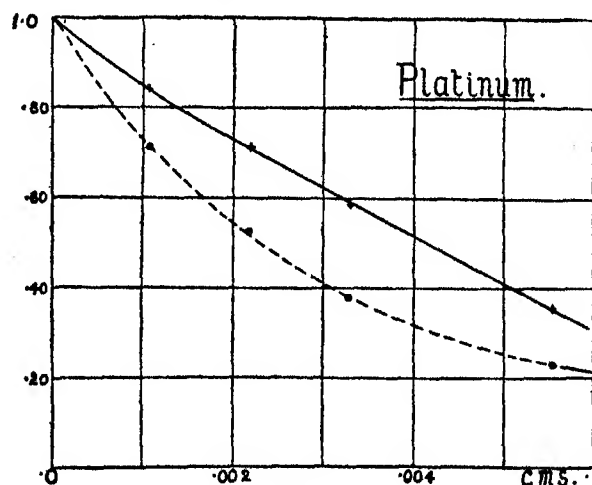


FIG. 6.

portion of the curve, that is to say, the portion corresponding to thicknesses less than 0.001 cm., the results connect themselves, as in the case of aluminium, with the experiments on scattering described above, the value of

* W. Wilson, 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 612.

$\phi/\sqrt{t_m}$ obtained from this portion being 27, as compared with the value 29 from the previous experiments.

After passing through 0.001 cm. of platinum, however, the absorption of the rays becomes exponential, as is shown by the unbroken curve in fig. 6, which gives the values of $\log_{10}(I/I_0)$ plotted against the corresponding values of t . Thus the absorption of homogeneous β -rays, after scattering in a thickness of only 0.001 cm. of platinum, follows the law which has always been found for the absorption of the rays from a single radioactive substance.

Table VII.—Absorption of the homogeneous β -rays by Aluminium after transmission through 0.001 cm. of Platinum.

t (cms.).	I/I_0 .	$\log_{10} I/I_0$.
0.0	1.00	—
0.020	0.70	1.84
0.048	0.41	1.61
0.061	0.31	1.49
0.081	0.22	1.34
0.110	0.12	1.08

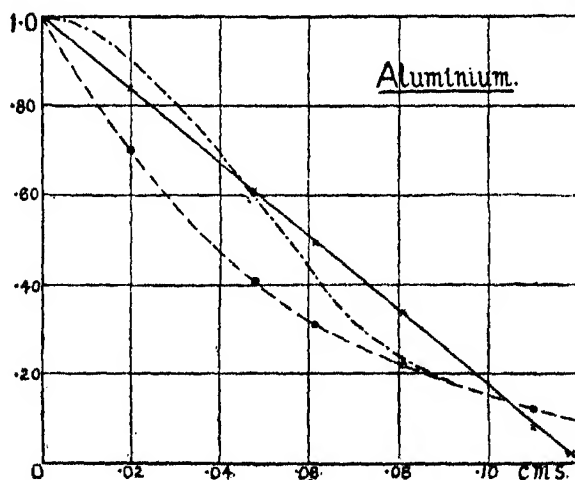


FIG. 7.

As a further test of this point, I have measured the absorption by aluminium of a beam of homogeneous β -rays which had first traversed a thin sheet of platinum. The results are given in Table VII, and graphically in fig. 7, where the full line gives the values of $\log_{10}(I/I_0)$ plotted against the thickness t . It will be seen that this is a straight line within the limits of experimental error. Thus the absorption in aluminium of homogeneous β -rays after previous scattering in 0.001 cm. of platinum follows an

exponential law. The lower dotted curve on the same diagram gives the actual values of I/I_0 , while for sake of comparison the absorption curve of fig. 5 is also reproduced on the same scale. It will be seen that these two curves eventually coincide. It seems probable, therefore, that the apparent difference in the results obtained for platinum and aluminium is one of degree only, and that, as suggested above, the homogeneous rays after scattering in aluminium also follow an exponential law of absorption. We are thus led to the conclusion that, while the scattering of a parallel pencil of homogeneous β -rays, and hence also the first stages in the absorption of a parallel pencil, takes place according to the laws considered in the first part of this paper, the absorption of the completely scattered beam follows an exponential law.

Wilson, who regarded his "linear" curves as giving the true law of absorption for homogeneous rays, has attempted to show that an exponential law of absorption is due to a peculiar distribution of velocities in the rays employed. It seems much more probable, however, from the above results that the exponential is the true absorption law for completely scattered β -radiation of uniform velocity, whether it emerges from a layer of radioactive material, or has been originally separated out by a magnetic field, and afterwards scattered in some absorbing substance.

In a recent paper Baeyer and Hahn* have published some excellent photographs of the magnetic spectra of various radioactive substances and their mixtures, from which it seems clear that the velocity of the β -rays emitted by any one radioactive substance, such as radium E, or the different thorium products, is, if not absolutely constant, at any rate confined within very narrow limits, and H. W. Schmidt† announces a similar result for the β -rays from uranium X, though Gray (in a paper recently read before this Society, the details of which are not to hand at the time of writing) has failed to observe any such effect.

It may be pointed out that the absorption coefficients obtained for platinum and aluminium after the scattering of the rays in platinum foil are in good agreement with the values to be expected from the velocity of the incident homogeneous rays. The velocity of the homogeneous beam used in these experiments was 2.68×10^{10} cm./sec., and the values obtained for λ/ρ (the coefficient of absorption divided by the density) for platinum and aluminium after the scattering of the rays were 11.9 and 6.9 respectively. The rays from uranium X, according to Schmidt,‡ have

* v. Baeyer and Hahn, 'Phys. Zeit.', 1910, vol. 11, p. 488.

† H. W. Schmidt, 'Phys. Zeit.', 1910, vol. 11, p. 265.

‡ H. W. Schmidt, 'Le Radium,' 1909, vol. 6, p. 5.

in which f denotes an arbitrary function. When u can be neglected in comparison with a , this reduces to the familiar law of undisturbed propagation applicable to infinitesimal waves.

Poisson does not discuss the significance of (3) further than to show that the boundaries of a continuous wave, limited to a finite range along x , are propagated with the ordinary velocity a , and that accordingly the length of the wave does not alter as it advances. The meaning of (3) is that in general u advances with a velocity equal, not to a , but to $a+u$, and that this might be expected is very easily seen (Earnshaw). From the ordinary theory we know that an infinitely small disturbance is propagated with a certain velocity a , which velocity is relative to the parts of the medium undisturbed by the wave. Let us consider now the case of a wave so long that the variations of velocity and density are insensible for a considerable distance along it, and at a place where the velocity (u) is finite let us imagine a small secondary wave to be superposed. The velocity with which the secondary wave is propagated through the surrounding medium is a , but on account of the local motion of the medium itself the whole velocity of advance is $a+u$, and depends upon the part of the long wave at which the small wave is placed. What has been said of the secondary wave applies also to the parts of the long wave itself, and thus we see that after a time t the place where a certain velocity u is to be found is in advance of its original position by a distance equal, not to at , but to $(a+u)t$, or, as we may express it, u is propagated with velocity $(a+u)$.

A closer discussion of the solution represented by Poisson's integral was given by Stokes,* who pointed out the difficulty which ultimately arises from the motion becoming discontinuous. If we draw a curve to represent the distribution of velocity, taking x for abscissa and u for ordinate, we may find the corresponding curve after the lapse of time t by the following construction:—Through any point on the original curve draw a straight line in the positive direction parallel to x , and of length equal to $(a+u)t$, or, as we are concerned with the shape of the curve only, equal to ut . The locus of the ends of these lines is the velocity-curve after a time t .

But this law of derivation cannot hold good indefinitely. The crests of the velocity-curve gain continually on the troughs and must at last overtake them. After this the curve would indicate two values of u for one value of x , ceasing to represent anything that could actually take place. In fact we are not at liberty to push the application of the integral beyond the point at which the velocity becomes discontinuous, or the velocity-curve has a vertical tangent. In order to find when this happens, let us take two

* "On a Difficulty in the Theory of Sound," 'Phil. Mag.,' November, 1846.

neighbouring points on any part of the curve which slopes downwards in the positive direction, and inquire after what time this part of the curve becomes vertical. If the difference of abscissæ be dx , the hinder point will overtake the forward point in the time $-dx/du$. Thus the motion, as determined by Poisson's integral, becomes discontinuous after a time equal to the reciprocal, taken positively, of the greatest negative value of du/dx .

For example, let us suppose that

$$u = U \cos \frac{2\pi}{\lambda} \{x - (a + u)t\}, \quad (4)$$

where U is the greatest initial velocity. When $t = 0$, the greatest negative value of du/dx is $-2\pi U/\lambda$, so that discontinuity will commence at the time $t = \lambda/2\pi U$.

The only kind of wave travelling in the positive direction which can escape ultimate discontinuity is one which has no forward slope. This is the case of a wave forming the transition between a larger constant value of u when x exceeds a certain value, and a smaller constant value when x falls short of a certain value. As time passes, the slope everywhere becomes easier. We shall see presently that this wave is a wave of rarefaction, in the sense that during its passage the gas passes from a greater to a less density.

It is worthy of remark that, although we may of course conceive a wave of finite disturbance to exist at any moment, there is in general a limit to the duration of its previous independent existence. By drawing lines in the negative instead of in the positive direction we may trace the history of the velocity-curve; and we see that as we push our inquiry further and further into past time the forward slopes become easier and the backward slopes steeper. At a time equal to the greatest positive value of dx/du , antecedent to that at which the curve is first contemplated, the velocity would be discontinuous. The exception is now a wave of condensation, involving a passage always from a less to a greater density.

When discontinuity sets in, a state of things exists to which the usual differential equations are inapplicable; and the subsequent progress of the motion has not been determined. It is probable, as suggested by Stokes, that some sort of reflection would ensue. In regard to this matter we must be careful to keep purely mathematical questions distinct from physical ones. We shall see later how the tendency to discontinuity may be held in check by forces of a dissipative character. But this has nothing directly to do with the mathematical problem of determining what would happen to waves of finite amplitude in a medium, free from viscosity, whose pressure is under all circumstances proportional to the density.* To suppose that the problem has

* 'Theory of Sound,' 1878, § 251.

no solution would seem to be tantamount to admitting an inherent contradiction in the assumption, usually made in hydrodynamics, of a continuous fluid subject to Boyle's law. It would be strange if the necessity of a molecular constitution for gases could be established by such an argument.

With Poisson's integral (3), showing how the velocity is propagated, there is associated another law connecting the velocity and the density in a positive progressive wave. In the case of a fluid obeying Boyle's law this relation is

$$u - a \log \rho = \text{const.} \quad (5)$$

It does not occur explicitly in Poisson's memoir, and Earnshaw considers that Poisson did not discover it. Certainly it is remarkable that he omitted to formulate the law, but at the same time it is difficult to suppose him ignorant of it, seeing that it follows by simple subtraction from two of his equations.* A formula equivalent to (5) was given explicitly, so far as I know, for the first time by Airy,† who attributes it to De Morgan.

The assumption that in a progressive wave there is a definite relation between u and ρ forms the basis of Earnshaw's investigation.‡ That such a relation is to be expected may be shown by a line of argument analogous to that already employed in connection with Poisson's integral.

Whatever may be the law of pressure as a function of density, the velocity of propagation of small disturbances is according to the usual theory equal to $\sqrt{(dp/d\rho)}$, and in a positive progressive wave the relation between velocity and condensation (s) is

$$u : s = \sqrt{(dp/d\rho)}, \quad (6)$$

where $s = \delta\rho/\rho$. If this relation be violated at any point, a wave will emerge, travelling in the negative direction. Let us now picture to ourselves the case of a positive progressive wave in which the changes of velocity and density are very gradual but become important by accumulation, and let us inquire what condition must be satisfied in order to prevent the formation of a negative wave. It is clear that the answer to the question whether or not a negative wave will be generated at any point will depend upon the state of things in the immediate neighbourhood of the point, and not upon the state of things at a distance from it, and will therefore be determined by the criterion applicable to small disturbances. In applying this criterion we are to consider the velocities and condensations, not absolutely, but relatively to

* Equations (1), p. 364, and (6), p. 367.

† 'Phil. Mag.,' 1849, vol. 34, p. 402. The corresponding formula for long tidal waves of finite amplitude was also given.

‡ 'Roy. Soc. Proc.,' January 6, 1859; 'Phil. Trans.,' 1860, p. 133.

those prevailing in the neighbouring parts of the medium, so that the form of (6) proper for the present purpose is

$$du = \sqrt{\left(\frac{dp}{d\rho}\right)} \cdot \frac{d\rho}{\rho}, \quad (7)$$

whence

$$u = \int \sqrt{\left(\frac{dp}{d\rho}\right)} \cdot \frac{d\rho}{\rho}, \quad (8)$$

which is the relation between u and ρ generally necessary for a positive progressive wave, as laid down by Earnshaw.*

Earnshaw worked with the so-called Lagrangian form of the equations, in which the motions of particular particles are followed, and he obtained complete solutions for a wave progressive in one direction. In the case of Boyle's law the relation between velocity and density is that already given (5), and in the case of the adiabatic law, where

$$\frac{p}{p_0} = \left(\frac{\rho}{\rho_0}\right)^\gamma, \quad (9)$$

Earnshaw finds

$$\left(\frac{\rho}{\rho_0}\right)^{\frac{1}{2}(\gamma-1)} = 1 + \frac{(\gamma-1)u}{2a}, \quad (10)$$

where a is the velocity of infinitesimal disturbances under the condition represented by p_0, ρ_0 , viz. $a^2 = \gamma p_0 / \rho_0$. In (9) γ denotes as usual the ratio of the two specific heats; and in (10), applicable to a *positive* progressive wave, the constant of integration has been so chosen that $u = 0$ corresponds to $\rho = \rho_0$.

The generalised form of Poisson's integral, appropriate when p is *any* given function of ρ , does not appear quite explicitly in Earnshaw's memoir. The line of argument already used shows that it must be

$$u = f[x - \{u + \sqrt{(dp/d\rho)}\} t]. \quad (11)$$

In the case of a gas obeying Boyle's law,

$$\sqrt{(dp/d\rho)} = \text{const.}, \quad (12)$$

and (11) reduces to Poisson's form.

In the case of the adiabatic law, we have from (9), (10),

$$\sqrt{\left(\frac{dp}{d\rho}\right)} = a \left(\frac{\rho}{\rho_0}\right)^{\frac{1}{2}(\gamma-1)} = a + \frac{\gamma-1}{2} u, \quad (13)$$

so that (Earnshaw)

$$u + \sqrt{(dp/d\rho)} = a + \frac{1}{2}(\gamma+1)u. \quad (14)$$

Thus (11) assumes the form

$$u = f[x - \{a + \frac{1}{2}(\gamma+1)u\} t], \quad (15)$$

and this with (10) may be considered to constitute the solution of the

* 'Theory of Sound,' 1878, § 261.

problem up to the point where discontinuity sets in. We may fall back upon Boyle's law by putting in (15) $\gamma = 1$.

It appears that whether the relation of pressure to density be isothermal or adiabatic, there is a change of type as the wave advances. There can be no escape from such a change unless $u + \sqrt{(dp/d\rho)}$ be constant. Using (8), we may deduce in this case

$$\sqrt{(dp/d\rho)} = B/\rho,$$

B being a constant, whence

$$p = A - B^2/\rho \quad (16)$$

expresses the only law of pressure under which waves of finite amplitude can be propagated without undergoing a change of type (Earnshaw). A simpler derivation of (16) will be given presently.

Earnshaw further considers the genesis of disturbance in a gas originally at rest by the motion of a piston (supposed to be contained in a tube), but some of his conclusions appear to need revision. All that is required in these problems is virtually contained in (8), (11). If X denote the position of the piston at time T , the velocity of its motion is $U = dX/dT$, and this velocity is shared by the gas in contact with it. On the positive side the velocity of propagation of U (equal to u) is, by (11),

$$U + \sqrt{(dp/d\rho)};$$

so that if at time t (greater than T), U is to be found at x , we must have

$$x = X + \{U + \sqrt{(dp/d\rho)}\} (t - T). \quad (17)$$

Among the problems which naturally suggest themselves would be to determine what happens when the piston originally at rest at $X = 0$ begins to move at time $T = 0$ with a constant velocity. But if this velocity be positive, the discontinuity, which immediately ensues, causes the failure of our equations. On the other hand, if the constant velocity be negative, say $-V$, the initial discontinuity disappears forthwith, and the subsequent motion may be traced.

Take, for example, the case of Boyle's law. We have

$$X = UT, \quad U + \sqrt{(dp/d\rho)} = U + a;$$

so that

$$x = Ut + a(t - T) \quad (t > T),$$

and we have to consider where the velocities 0 and $-V$ are to be found at time t . Now $U = 0$ corresponds to the range of T from $-\infty$ to 0, so that x ranges from at to ∞ . Again, $U = -V$ corresponds to the range of T from 0 to t , so that x ranges from $(a - V)t$ to $-Vt$. The whole range of x on the positive side of the piston is now accounted for, except the interval from $x = (a - V)t$ to $x = at$. This is occupied by the transition of velocity

from 0 to $-V$, and we infer, from what was said in the discussion of Poisson's integral, that this transition must take place linearly.

Under Boyle's law the relation between velocity and density (5) is such that, however fast the piston may recede (u negative), a complete vacuum can never be formed behind it. It is otherwise under the adiabatic law (10), where $\rho = 0$ corresponds to

$$u = -2a/(\gamma - 1) \quad (\text{Earnshaw}).$$

It may be of interest to consider further a few examples of (17). Still assuming Boyle's law, let us suppose that the piston is at rest ($X = 0$) until $T = 0$, and then moves with uniform acceleration (g), so that ($T +$)

$$U = gT, \quad X = \frac{1}{2} gT^2 = U^2/2g.$$

The use of these in (17) gives

$$x = \frac{a^2}{2g} + (U + a)t - \frac{(U + a)^2}{2g}, \quad (18)$$

showing that the relation between x and U is parabolic. In (18) we see that dx/dU vanishes, when $t = (U + a)/g$. Thus, if g be positive, i.e. if the wave be one of condensation, discontinuity sets in at the front after an interval, reckoned from the beginning of the motion, equal to a/g . But if g be negative, there is no discontinuity, and (18) remains valid for an indefinite time.

In general, as in the last example ($g +$), the discontinuity sets in locally at one point of the velocity-curve, while other parts are temporarily exempt. It is of interest to inquire under what law the piston must advance so as to generate a linear velocity-curve. For then, under the adiabatic law, which includes Boyle's, a velocity-curve, once linear, remains linear, and if discontinuity enters, it must affect the whole curve simultaneously.

It may be worth while to pause here for a moment to inquire what law of pressure is implied in the permanence of the linear character of the velocity-curve. By (7)

$$\rho \frac{du}{d\rho} = \sqrt{\left(\frac{dp}{d\rho}\right)};$$

so that if $u + \sqrt{(dp/d\rho)}$ is a linear function of u , $du/d\log\rho$ must also be a linear function of u . This requires that

$$\rho du/d\rho = C\rho^n,$$

where C and n are constants, and the most general relation between p and ρ consistent with the requirements is

$$p = A + B\rho^\gamma, \quad (19)$$

where A , B , γ , are constants. The relation (19) may be regarded as a kind

of generalised adiabatic law; it includes the special law (16) under which a velocity-curve is absolutely permanent in type.

Supposing the motion to commence at $T = 0$, we have

$$X = \int_0^T U dT = UT - \int_0^U T dU,$$

and hence from (17), under the supposition of Boyle's law,

$$x = -\int T dU - (U + a)t - aT; \quad (20)$$

and the question before us is so to determine T as a function of U that (20) may be linear in U . From (20) when t is constant

$$\frac{dx}{dU} = -T + t - a \frac{dT}{dU} = t_0, \text{ say,}$$

where t_0 is a constant, whence

$$T = t - t_0 + H e^{-U/a},$$

H being the constant of integration. But, since $U = 0$ when $T = 0$, this assumes the form

$$T = T' (1 - e^{-U/a}), \quad (21)$$

T' being written for $t - t_0$. Or, if we express U in terms of T ,

$$U = -a \log \left(1 - \frac{T}{T'} \right). \quad (22)$$

In (21), (22), T' is positive, if U is positive; and U becomes infinite when $T = T'$. We must therefore regard the law as limited to values of T less than T' .

From (22) we find

$$X = \int_0^T U dT = a \left\{ (T' - T) \log \left(1 - \frac{T}{T'} \right) + T \right\}, \quad (23)$$

which completely expresses the motion of the piston. The corresponding velocity-curve at time t may be verified by means of (20), (21). It is expressed by

$$U = \frac{at - x}{T' - t}, \quad (24)$$

exhibiting the linear character of the slope of velocity. Evidently the slope becomes vertical throughout when $t = T'$.

In the above example it is not necessary to suppose the law of motion of the piston continued up to $T = T'$. On the contrary, we may imagine U to increase up to some prescribed finite value and then to remain constant. In this case the slope expressed by (24) forms the transition between $U = 0$ for values of x greater than at and the finite value at which the acceleration of the piston stops.

If the wave be one of rarefaction we must take T' negative, say $-T''$. In this case the analogue of (22) shows that U constantly increases in numerical value but does not become infinite in any finite time. The analogue of (24) is

$$U = \frac{x - at}{t + T''}, \quad (25)$$

representing a slope which ever grows easier as time passes.

The problem also admits of solution when the gas follows the adiabatic law (9). As in (15), (20),

$$x = X + \left\{a + \frac{1}{2}(\gamma + 1)U\right\}(t - T); \quad (26)$$

and (26) is to satisfy the condition of making dx/dU constant. In this

$$dX/dU = U \cdot dT/dU,$$

so that
$$\frac{dT}{dU} \{(\gamma - 1)U + 2a\} + (\gamma + 1)(T - t) = \text{const.}$$

On integration we obtain, under the condition that U and T vanish together,

$$\left(1 - \frac{T}{T'}\right) \left[1 + \frac{\gamma - 1}{2a}U\right]^{\frac{\gamma + 1}{\gamma - 1}} = 1, \quad (27)$$

T' being a constant which, if positive, corresponds to $U = \infty$, thereby determining U as a function of T .

For the value of $X = \int_0^T U dT$, we have

$$\begin{aligned} \frac{\gamma - 1}{2a} \frac{X}{T'} &= -\frac{\gamma + 1}{2} \left[\left(1 - \frac{T}{T'}\right)^{\frac{2}{\gamma - 1}} - 1 \right] - \frac{T}{T'} \\ &= \frac{\gamma - 1}{2} - \frac{\gamma + 1}{2} \left(1 + \frac{\gamma - 1}{2a}U\right)^{-\frac{2}{\gamma - 1}} + \left(1 + \frac{\gamma - 1}{2a}U\right)^{-\frac{\gamma + 1}{\gamma - 1}}. \end{aligned} \quad (28)$$

It may be observed that, although U is infinite when $T = T'$, X remains finite. Using this in (26), we get finally, on reduction,

$$x = at - \frac{1}{2}(\gamma + 1)U(T' - t), \quad (29)$$

or
$$U = \frac{2}{\gamma + 1} \frac{at - x}{T' - t}. \quad (30)$$

If $x < at$, U is a linear function of x , and (T' being positive) the slope of the velocity curve increases until it becomes vertical when $t = T'$.

If T' is negative, the wave is one of rarefaction, and (30) applies however great t may be.

By putting $\gamma = 1$ we fall back from (30) to (24), and less simply from (28) to (23).*

* I have since found that this problem was successfully treated by Hugoniot.

Riemann's work* is of somewhat later date than Earnshaw's, but in one important respect is more general. It may be convenient briefly to recall the principal result.

Taking p a given function of ρ , say $\phi(\rho)$, and putting $X = 0$, we have from (1) and (2)

$$\frac{du}{dt} + u \frac{du}{dx} = -\phi'(\rho) \frac{d \log \rho}{dx}, \quad \frac{d \log \rho}{dt} + u \frac{d \log \rho}{dx} = -\frac{du}{dx}.$$

If the second of these equations be multiplied by $\pm \sqrt{\phi'(\rho)}$ and be added to the first, we find

$$\frac{dr}{dt} = -\{u + \sqrt{\phi'(\rho)}\} \frac{dr}{dx}, \quad \frac{ds}{dt} = -\{u - \sqrt{\phi'(\rho)}\} \frac{ds}{dx}, \quad (31)$$

$$\text{where} \quad 2r = f(\rho) + u, \quad 2s = f(\rho) - u, \quad (32)$$

$$\text{and} \quad f(\rho) = \int \sqrt{\phi'(\rho)} \cdot d \log \rho. \quad (33)$$

From these follow

$$dr = \frac{dr}{dx} [dx - \{u + \sqrt{\phi'(\rho)}\} dt]$$

$$ds = \frac{ds}{dx} [dx - \{u - \sqrt{\phi'(\rho)}\} dt];$$

so that r remains constant when x and t change in such a manner that $dx = \{u + \sqrt{\phi'(\rho)}\} dt$, and s remains constant when x and t change so that $dx = \{u - \sqrt{\phi'(\rho)}\} dt$. In the case of a positive progressive wave $s = 0$, whence $f(\rho) = u$ and also $r = u$. The velocity with which u travels in such a wave is accordingly $u + \sqrt{dp/d\rho}$, of which fact (11) is merely another form of statement. Riemann's equations are more general than anything previously given, as not limited to a single progressive wave.

Since Riemann's equations do not seem to have been applied in any example of continuous motion, I have thought it worth while to inquire whether they can be satisfied when r and s are both linear functions of x , Boyle's law being assumed, so that in (32), (33)

$$\sqrt{\phi'(\rho)} = a, \quad f(\rho) = a \log \rho.$$

If we suppose

$$r = Ax + B, \quad s = Cx + D, \quad (34)$$

we obtain, on substitution in (31), equations for the determination of A , B , C , D , as functions of the time. In the first instance we find

$$A - C = 1/t, \quad (35)$$

in which to t a constant may be added, and further

$$A = \frac{H+1}{2t}, \quad C = \frac{H-1}{2t}, \quad (36)$$

* 'Göttingen Abhandlungen,' 1860, vol. 8.

when H is an arbitrary constant. Also

$$B - D = -aH + L/t, \quad (37)$$

L being another arbitrary constant, and thence

$$B = \frac{1}{2}a(H^2 - 1) \log t + \frac{L(H+1)}{2t} + \frac{1}{2}M, \quad (38)$$

$$D = \frac{1}{2}a(H^2 - 1) \log t + \frac{L(H-1)}{2t} + \frac{1}{2}N, \quad (39)$$

with

$$M - N = -2aH. \quad (40)$$

If we allow the origin of x to be arbitrary, as well as that of t , we may write

$$2r = (H+1)x/t + (H^2-1)a \log t + M, \quad (41)$$

$$2s = (H-1)x/t + (H^2-1)a \log t + N, \quad (42)$$

$$u = r - s = x/t - aH, \quad (43)$$

$$a \log \rho = r + s = Hx/t + (H^2-1)a \log t + \frac{1}{2}(M+N). \quad (44)$$

If $H = \pm 1$, the logarithmic term disappears, and either r or s is constant. In these cases we fall back upon single progressive waves.

If $H = 0$, $u = x/t$ in (43), and (44) gives $1/\rho$ proportional to t . The density is thus uniform with respect to x , but the volume of a given mass grows proportionally with t . The uniform expansion occurs in such a manner that the gas remains unmoved at the origin of co-ordinates. Since in this case $du/dt + u du/dx = 0$, we see that every part of the gas moves with unaccelerated velocity.

Waves of Permanent Regime.

When waves are propagated in one dimension without change of type, the circumstances are dynamically the same as in steady motion, as appears at once by impressing on the system a velocity equal and opposite to that of wave-propagation. The problem may conveniently be considered under this form.

From the general equation of continuity (2), by making $d\rho/dt$ equal to zero, or independently, we have

$$\rho u = \rho_0 u_0 = m, \quad (45)$$

where m is a constant which Rankine called the mass-velocity. The dynamical equation (1) reduces to

$$u \frac{du}{dx} + \frac{1}{\rho} \frac{dp}{dx} = X. \quad (46)$$

If $X = 0$, (46) may be written

$$\int_{p_0}^p \frac{dp}{\rho} = \frac{1}{2} u_0^2 - \frac{1}{2} u^2, \quad (47)$$

where u_0 is the velocity corresponding to p_0 .

Eliminating u , we get

$$\int_{p_0}^p \frac{dp}{\rho} = \frac{1}{2} u_0^2 \left(1 - \frac{\rho_0^2}{\rho^2} \right), \quad (48)$$

determining the law of pressure under which alone it is possible for a stationary wave to maintain itself in fluid moving (outside the wave) with velocity u_0 . From (48)

$$\frac{dp}{d\rho} = u_0^2 \frac{\rho_0^2}{\rho^2}, \quad (49)$$

or

$$p + m^2/\rho = p_0 + m^2/\rho_0, \quad (50)$$

the law found by Earnshaw.

Since, under the adiabatic law, the relation between density and pressure differs from (50), we conclude that a self-maintaining stationary aerial wave is an impossibility, unless it be in virtue of impressed forces, or of viscosity, or other dissipative agencies not now regarded.

When the changes of density concerned are *small*, (50) may be satisfied approximately; and we see from (49) that the velocity of the stream (outside the wave) necessary to keep the wave stationary is given by

$$u_0 = \sqrt{(dp/d\rho)},$$

which is the same as the velocity of the wave reckoned relatively to the fluid at a distance.

This way of regarding the subject shows, perhaps more clearly than any other, the nature of the relation between velocity and density. In a stationary wave-form a loss of velocity accompanies an augmented density, according to the principle of energy, and therefore the fluid composing the condensed parts of a wave moves forward more slowly than the undisturbed portions. Relatively to the fluid at a distance, the motion of the condensed parts is in the same direction as that in which the waves travel.

By means of (46), we can find what impressed force is required in order to ensure a stationary wave-form when (50) is not satisfied. For example, if $p = a^2\rho$, we find from (45), (46),

$$X = u \frac{du}{dx} + a^2 \frac{d \log \rho}{dx} = (u^2 - a^2) \frac{d \log u}{dx}, \quad (51)$$

showing that an impressed force is necessary at every place where u is variable and unequal to a . In (51) X is the accelerating force so called.

The actual force operative upon the element of mass ρdx is $X\rho dx$. Thus, on integration,

$$\int X\rho dx = m \int \left(1 - \frac{a^2}{u^2}\right) du = m(u_2 - u_1) \left\{1 - \frac{a^2}{u_1 u_2}\right\}, \quad (52)$$

if the range of integration extend from the place where the velocity is u_1 to the place where it becomes equal to u_2 . The integral applied force vanishes if the terminal velocities are such that their geometric mean is a . We may apply this to the case of a velocity-curve giving a simple gradual transition from one constant velocity u_1 to another constant velocity u_2 . Under the above condition the integral force vanishes, but finite forces are required at all points of the slope, except the particular point where $u = a$.

It is of some importance to notice that although, under the condition $u_1 u_2 = a^2$, the applied forces contribute on the whole no *momentum*, yet they do contribute *energy*, positive or negative. To find the work done in unit of time by the forces we have

$$2/m \cdot \int X\rho \cdot u \cdot dx = u_2^2 - u_1^2 - 2u_1 u_2 \log(u_2/u_1). \quad (53)$$

The better to interpret this let us suppose that u_1 and u_2 are positive, and in the first instance that $u_2 > u_1$, so that the fluid passes from a less to a greater velocity, or by (45) from a greater to a less density. In the case of a wave of rarefaction we have therefore to consider the sign of

$$y^2 - 1 - 2y \log y, \quad (54)$$

when $y > 1$. It is not difficult to prove that this sign is always positive. When $y - 1$ is small, the approximate value of (54) is $\frac{1}{3}(y - 1)^3$, and is therefore positive when $y > 1$. Again, if we remove the positive factor y from (54) and then differentiate, we obtain $(1 - 1/y)^2$, which is positive. Hence, when $y > 1$, (54) is necessarily positive. The propagation of the wave of rarefaction without change of type requires that the impressed forces, contributing on the whole no momentum, should nevertheless do work upon, *i.e.* communicate energy to, the gas.

In like manner, if the wave be one of condensation, *i.e.*, if the gas passes from a less to a greater density, the operation of the impressed forces is to remove energy from the gas forming the wave. It follows that although dissipative forces, such as those arising from viscosity, may possibly constitute a machinery capable of maintaining the type of a wave of condensation, in no case can they maintain the type of a wave of rarefaction.

It is desirable to extend this argument to waves propagated under the adiabatic law. In general, from (45), (46),

$$X\rho = m \frac{du}{dx} + \frac{dp}{dx};$$

so that $\int X\rho dx = m(u_2 - u_1) + p_2 - p_1 = m^2/\rho_2 - m^2/\rho_1 + p_2 - p_1$.

As in (50), the condition that on the whole no momentum is communicated is

$$m^2/\rho_2 - m^2/\rho_1 + p_2 - p_1 = 0. \quad (55)$$

Again,

$$m^{-1} \cdot \int X \rho \cdot u \cdot dx = \frac{1}{2} (u_2^2 - u_1^2) + \int_{p_1}^{p_2} \frac{dp}{\rho} = \int_{p_1}^{p_2} \frac{dp}{\rho} - \frac{p_2 - p_1}{2} \left(\frac{1}{\rho_2} + \frac{1}{\rho_1} \right). \quad (56)$$

The question in which we are interested is the sign of (56). If we regard v (the volume of unit mass), viz., $1/\rho$, as the ordinate, and p as the abscissa of a curve, the first term on the right of (56) represents the area of the curve bounded by two ordinates and the axis of p , while the second term is what the area would be if the ordinate retained throughout the mean of the terminal values.

So far the argument is general. If the relation between p and v be adiabatic, and $p_2 > p_1$, the expression (56) is negative, since v proportional to $p^{-1/\gamma}$ makes d^2v/dp^2 positive.* The final pressure exceeding the initial pressure denotes a wave of condensation, and we conclude, as before, that maintenance of type in such a wave requires removal of energy from the wave, while in the contrary case of a wave of rarefaction additional energy would need to be supplied.

The problem now under discussion is closely related to one which has given rise to a serious difference of opinion. In his paper of 1848 already referred to, Stokes considered the *sudden* transition from one constant velocity to another, and concluded that the necessary conditions for a permanent regime could be satisfied. Results equivalent to his may be deduced from (45) in connection with the condition ($u_1 u_2 = a^2$) already found from (52) to express that there is no change of momentum on the whole. Thus,

$$u_1 = a\sqrt{(\rho_2/\rho_1)}, \quad u_2 = a\sqrt{(\rho_1/\rho_2)}. \quad (57)$$

Similar conclusions were put forward by Riemann in 1860 (*loc. cit.*). Commenting on these results in the "Theory of Sound" (1878), I pointed out that although the conditions of *mass* and *momentum* were satisfied, the condition of *energy* was violated, and that therefore the motion was not possible; and in republishing this paper† Stokes admitted the criticism, which had indeed already been made privately by Kelvin. On the other hand, Burton‡ and H. Weber§ maintain, at least to some extent, the original view.

* Compare Lamb's 'Hydrodynamics,' § 280.

† 'Collected Works,' vol. 2, p. 55.

‡ 'Phil. Mag.,' 1893, vol. 35, p. 316.

§ 'Die Partiellen Differentialgleichungen der Mathematischen Physik,' Braunschweig, 1901, vol. 2, p. 496.

Inasmuch as they ignored the question of energy, it was natural that Stokes and Riemann made no distinction between the cases where energy is gained or lost. As I understand, Weber abandons Riemann's solution for the discontinuous wave (or *bore*, as it is sometimes called for brevity) of rarefaction, but still maintains it for the case of the bore of condensation. No doubt there is an important distinction between the two cases; nevertheless, I fail to understand how a loss of energy can be admitted in a motion which is supposed to be subject to the isothermal or adiabatic laws, in which no dissipative action is contemplated. In the present paper the discussion proceeds upon the supposition of a *gradual* transition between the two velocities or densities. It does not appear how a solution which violates mechanical principles, however rapid the transition, can become valid when the transition is supposed to become absolutely abrupt. All that I am able to admit is that under these circumstances dissipative forces (such as viscosity) that are infinitely small may be competent to produce a finite effect.

If we suppose that under the influence of small dissipative forces the bore of Stokes and Riemann can be propagated, at least approximately, we naturally inquire whether it can be regarded as the complete outcome of the simple progressive wave with a straight velocity slope which, as we have found, tends after a definite interval of time to assume the character of a bore. It would seem that the answer must be in the negative. Taking Boyle's law, we recognise from (5) that in the progressive wave, just before the formation of the bore, the relation between the velocities and densities is

$$u_2 - u_1 = a \log \rho_2 - a \log \rho_1,$$

while in (57) the relation is

$$u_2 - u_1 = a\sqrt{(\rho_2/\rho_1)} - a\sqrt{(\rho_1/\rho_2)}.$$

The two functions of ρ on the right, which are independent of any common addition to u_1 and u_2 , cannot be identified (unless $\rho_2 = \rho_1$), as we have found already in discussing (54). This incompatibility may be regarded as a confirmation of Stokes' opinion that something of the nature of reflection must ensue.

Permanent Regime under the influence of Dissipative Forces.

The first investigation to be considered under this head is a very remarkable one by Rankine "On the Thermodynamic Theory of Waves of Finite Longitudinal Disturbance,"* which (except a limited part expounded

* 'Phil. Trans,' 1870, vol. 180, Part II, p. 277.

by Maxwell in his "Theory of Heat") has been much neglected.* Conduction of heat is here for the first time taken into account and although there are one or two serious deficiencies, not to say errors, presently to be noticed, the memoir marks a very definite advance.

The first step is the establishment of an equation equivalent (when the wave is reduced to rest) to (45), and of Earnshaw's relation (50), in which equations we shall usually substitute v , the volume of unit mass, for $1/\rho$. Rankine remarks that "no substance yet known fulfils the condition expressed by (50) between finite limits of disturbance, at a constant temperature, nor in a state of non-conduction of heat (called the *adiabatic* state). In order, then, that permanency of type may be possible in a wave of longitudinal disturbance, there must be both change of temperature and conduction of heat during the disturbance." However, we shall see later that even under Boyle's law *viscosity* is competent to endow a wave with permanency.

The question is, how can Earnshaw's law be satisfied? Obviously not (in the absence of viscosity) if the expansions are adiabatic; but if at every stage the right quantity of heat is added or subtracted, the gas may be made to follow any prescribed law. This is the idea underlying Rankine's investigation. For the unit mass of a *perfect gas* we have, as usual, $p v = R \theta$, θ denoting absolute temperature. The condition of the gas is defined by any two of the three quantities p , v , θ , and the third may be expressed in terms of them. The relation between simultaneous variations is

$$d\theta/\theta = dp/p + dv/v. \quad (58)$$

In order to effect the changes specified by dp and dv , it is in general necessary to communicate heat to the gas. Calling the necessary quantity of heat dQ , we may write

$$dQ = \left(\frac{dQ}{dv}\right) dv + \left(\frac{dQ}{dp}\right) dp. \quad (59)$$

Suppose now (a) that $dp = 0$. Equations (58), (59), give

$$\frac{dQ}{d\theta} (p \text{ constant}) = \left(\frac{dQ}{dv}\right) \frac{v}{\theta},$$

where $dQ/d\theta$ (p constant) expresses the specific heat of the gas under constant pressure. Denoting this by C , we have

$$C = \left(\frac{dQ}{dv}\right) \frac{v}{\theta}.$$

* I must take my share of the blame. Rankine is referred to by Lamb ('Hydrodynamics,' 1906, p. 466). The body of Rankine's memoir seems to have been composed without acquaintance with the writings of his predecessors; but in a supplement he notices the work of Poisson, Stokes, Airy, and Earnshaw.

Again, suppose (b) that $dv = 0$. We find in a similar manner that if c denote the specific heat under constant volume,

$$c = \left(\frac{dQ}{dp} \right) \frac{p}{\theta}.$$

Thus, in general, $dQ/\theta = Cdv/v + cdp/p$. (60)

If between (58) and (60) we eliminate dp , there results

$$dQ = (C - c) \frac{p dv}{R} + cd\theta. \quad (61)$$

In (61) $dQ = 0$ corresponds to adiabatic expansion, when according to Mayer's principle the cooling effect $-cd\theta$ is equal to the external work done by the gas $p dv$. Hence

$$C - c = R, \quad (62)$$

and therefore $\gamma = \frac{C}{c} = \frac{C}{C - R}$, (63)

a relation discovered by Rankine himself in 1850.

Rankine then applies (60) to find what heat must be communicated in order that the gas may follow Earnshaw's law making $dp = -m^2 dv$. With regard to (62), it appears that

$$dQ = \frac{dp}{m^2(\gamma - 1)} \{p_0 + m^2 v_0 - (\gamma + 1)p\}. \quad (64)$$

It will be understood that under the condition now imposed of Earnshaw's relation, as well as of the ordinary gas law, there remains but one independent variable, and that the state of the gas may be expressed in terms of any *one* of the three quantities p , v , θ .

We have next to consider how far the necessary supply of heat defined by (64) can be effected by *conduction*. If the initial state (distinguished by suffix 1) and final state (with suffix 2) be of uniformity with respect to x , the total quantity of heat received by the gas during its passage must be zero, or $\int dQ = 0$. Hence from (64) Rankine finds

$$p_0 + m^2 v_0 = \frac{1}{2}(\gamma + 1)(p_1 + p_2). \quad (65)$$

This is a necessary condition; but of course there is nothing so far to show that it is sufficient.

In (65) p_0 , v_0 are any corresponding values of p and v within the wave, and we may identify them with p_1 , v_1 .*

Thus

$$m^2 v_1 = \frac{1}{2}(\gamma - 1)p_1 + \frac{1}{2}(\gamma + 1)p_2. \quad (66)$$

* We may, of course, also identify p_0 , v_0 with p_2 , v_2 .

The velocity u_1 , equal to mv_1 , is that with which the wave advances relatively to the fluid in state (1). And

$$u_1^2 = m^2 v_1^2 = v_1 \left\{ \frac{1}{2}(\gamma-1)p_1 + \frac{1}{2}(\gamma+1)p_2 \right\} \quad (67)$$

gives the square of the velocity of wave-propagation relatively to fluid (1). The velocity of propagation of infinitely small disturbances (p_2 nearly equal to p_1) is given by $u_1^2 = \gamma p_1 v_1$; and thus a wave of finite condensation is propagated faster than an infinitesimal wave, and according to (67) a wave of finite rarefaction would be propagated slower than an infinitesimal wave. Moreover, there is no limit to the velocity of a wave of condensation.

Rankine proceeds to express the absolute temperature (θ) at a point where the pressure is p in a wave of permanent type. By Earnshaw's law (50) in combination with (65)

$$\frac{\theta}{\theta_0} = \frac{pv}{p_0 v_0} = \frac{p}{p_0} \cdot \frac{(\gamma+1)(p_1+p_2)-2p}{(\gamma+1)(p_1+p_2)-2p_0}, \quad (68)$$

and for the ratio of terminal temperatures

$$\frac{\theta_2}{\theta_1} = \frac{p_2}{p_1} \cdot \frac{(\gamma+1)p_1 + (\gamma-1)p_2}{(\gamma+1)p_2 + (\gamma-1)p_1}. \quad (69)$$

The second fraction on the right of (69) obviously represents the ratio of volumes v_2/v_1 , or of densities ρ_1/ρ_2 .

In order to justify (65), it is not necessary that the terminal states be states of absolute uniformity. It will suffice that the temperature be there stationary ($d\theta/dx = 0$), which secures that no conduction of heat takes place there, and a state of stationary temperature usually involves a stationary pressure. To make the most of (65) we must apply it to the smallest ranges, *i.e.* between consecutive places where dp/dx vanishes.

But here a question arises which Rankine does not seem to have considered. In order to secure the necessary transfers of heat by means of conduction it is an indispensable condition that the heat should pass from the hotter to the colder body. If maintenance of type be possible in a particular wave as the result of conduction, a reversal of the motion will give a wave whose type cannot be so maintained. We have seen reason already for the conclusion that a dissipative agency can serve to maintain the type only when the gas passes from a less to a more condensed state. If this be so, the application which Rankine makes to a periodic wave is evidently prohibited.

According to the *second* law of thermodynamics, the criterion whether the transformation is possible as the result of dissipative action is the sign of

$\int dQ/\theta$. If this be negative, the transformation is not possible. From (64) with use of (65)

$$dQ = \frac{(\gamma+1)dp}{2m^2(\gamma-1)}(p_1+p_2-2p). \quad (70)$$

In (68) we may give p_0, θ_0 any corresponding values found in the wave. Thus p_0 lies between p_1 and p_2 , and $(\gamma > 1)$

$$(\gamma+1)(p_1+p_2)-2p_0 \text{ is positive.}$$

Accordingly $\int dQ/\theta$ takes the same sign as

$$\int_{p_1}^{p_2} \frac{dp(p_1+p_2-p)}{p\{(\gamma+1)(p_1+p_2)-2p\}}. \quad (71)$$

The integral (71) is evaluated without difficulty. Dropping the factor $1/(\gamma+1)$, and writing $\varpi = p_2/p_1$, we get

$$\log \varpi + \gamma \log \frac{\gamma+1+(\gamma-1)\varpi}{\gamma-1+(\gamma+1)\varpi}. \quad (72)$$

It is evident that (72) changes sign when we substitute $1/\varpi$ for ϖ .

If we expand (72) in powers of $(\varpi-1)$ we find

$$(72) = \frac{(\gamma^2-1)(\varpi-1)^3}{12\gamma^3} + \dots,$$

the terms in $(\varpi-1), (\varpi-1)^2$, disappearing. Thus, when $\varpi-1$ is positive, (72) begins positive. Differentiating (72) with respect to ϖ , we get

$$\frac{1}{\varpi} + \frac{\gamma(\gamma-1)}{\gamma+1+(\gamma-1)\varpi} - \frac{\gamma(\gamma+1)}{\gamma-1+(\gamma+1)\varpi}. \quad (73)$$

When (73) is reduced to a single fraction, the denominator is positive, and the numerator is

$$(\gamma^2-1)(\varpi-1)^2.$$

We infer that if $\varpi > 1$, (72) is always positive, and that if $\varpi < 1$, (72) is always negative. Hence if $p_2 > p_1$, i.e. if the wave be one of condensation, the communications of heat required are such as may arise from conduction; but if the wave be one of rarefaction, its permanency can in no wise be attained as the result of conduction. A wave of condensation here means a wave such that during its progress the gas passes always from a less dense to a more dense state, and the most important case is when the limits are finite, so that the passage constitutes the transition from one uniform density to a greater uniform density.

Rankine proceeds to examine more particularly under what conditions a wave can be permanent. "In order that a particular type of disturbance may be capable of permanence during its propagation, a relation must exist between the temperatures of the particles and their relative positions, such

that the conduction of heat between the particles may effect the transfers of heat required by the thermodynamic conditions of permanence of type."

The equation of conduction is readily found. The heat conducted in unit time across a layer of the gas is represented by $k \frac{d\theta}{dx}$, where k is a coefficient of conductivity which may be a function of the condition of the gas, here dependent on one variable. The equation of conduction is ($u = +$)

$$v \frac{d}{dx} \left(k \frac{d\theta}{dx} \right) = \frac{D}{Dt} Q = u \frac{dQ}{dx} = mv \frac{dQ}{dx},$$

whence, if we reckon Q from the initial condition of constant pressure p_1 ,

$$k \frac{d\theta}{dx} = mQ. \quad (74)$$

And from (70)

$$Q = \frac{\gamma+1}{2m^2(\gamma-1)} \int_{p_1}^p (p_1+p_2-2p) dp = \frac{\gamma+1}{2m^2(\gamma-1)} (p-p_1)(p_2-p). \quad (75)$$

Also from (50), (65),

$$p + m^2v = \frac{1}{2}(\gamma+1)(p_1+p_2), \quad (76)$$

whence

$$\theta = \frac{pv}{R} = \frac{p}{2m^2R} \{(\gamma+1)(p_1+p_2)-2p\}, \quad (77)$$

and

$$\frac{d\theta}{dp} = \frac{(\gamma+1)(p_1+p_2)-4p}{2m^2R}. \quad (78)$$

Using these, we find with regard to (62)

$$dx = \frac{k}{mQ} \frac{d\theta}{dp} dp = \frac{k dp}{mc(\gamma+1)} \frac{(\gamma+1)(p_1+p_2)-4p}{(p-p_1)(p_2-p)}, \quad (79)$$

by which is determined the distribution of pressure (and thence of density and temperature) along the line of propagation.

On the supposition that k is constant, Rankine integrates (79) in terms of logarithms. Writing

$$p - \frac{1}{2}(p_1+p_2) = q, \quad \frac{1}{2}(p_2-p_1) = q_1,$$

he obtains

$$\frac{dx}{dq} = \frac{k}{mc(\gamma+1)} \frac{(\gamma-1)(p_1+p_2)-q}{q_1^2-q^2},$$

$$\text{and} \quad x = \frac{k}{mc(\gamma+1)} \left\{ \frac{(\gamma-1)(p_1+p_2)}{2q_1} \log \frac{q_1+q}{q_1-q} + 2 \log \left(1 - \frac{q^2}{q_1^2} \right) \right\}, \quad (80)$$

x being measured from the place where $q = 0$. Mathematically the wave is infinitely long; but practically the transition of pressure is effected in a distance comparable with $k/mc(\gamma+1)$, which may be small in terms of ordinary standards. It is to be observed that the general character of the result does not depend upon the constancy of k .

Reverting to (79), we see that the denominator on the right is positive, and

that the numerator is also positive for that part of the wave where p is nearly equal to $\frac{1}{2}(p_1 + p_2)$. Thus, for this part of the wave at any rate, p and x increase together; or, since u is positive, the gas passes to a condition of greater density—the wave must be one of condensation. This consideration, as we have seen, Rankine overlooked. And a further limitation presents itself: since there cannot be two pressures in one place, it is evident that dx/dp must not change sign. The numerator in (79) must be positive over its *whole* range from p_1 to p_2 , and this will not be the case if p_2/p_1 exceed $(\gamma + 1)/(3 - \gamma)$, equal for common gases to 1.61. The conclusion is that the only kind of wave, involving a transition from one uniform pressure to another, which can be maintained with the aid of conduction is a wave of condensation, and then only when the ratio of pressures does not exceed a moderate value.

The next contribution to the subject upon which I have to comment is contained in a long and ably written memoir by Hugoniot.* This author, though he covers to a great extent the same ground, makes no reference to Stokes, Earnshaw, Riemann, or Rankine, and but a very slight one to Poisson—a circumstance which increases the difficulty of comparison. Since Hugoniot uses the Lagrangian form of equation, his investigation runs naturally on the same lines as Earnshaw's, whose general solution for a single progressive wave is reproduced. I have already alluded to the solution of special problems relating to the propagation of a wave of variable type.

The most original part of Hugoniot's work has been supposed to be his treatment of discontinuous waves involving a sudden change of pressure, with respect to which he formulated a law often called after his name by French writers. But a little examination reveals that this law is *precisely the same* as that given 15 years earlier by Rankine, a fact which is the more surprising inasmuch as the two authors start from quite different points of view. Rankine's investigation, as we have seen, is expressly based upon conduction of heat in the gas, but Hugoniot supposes his gas to be non-conducting. A question of some delicacy is here involved, which will repay careful examination. It will be convenient to give a paraphrase of Hugoniot's argument.†

This argument depends upon an application of the principle of energy to a region bounded by two fixed planes, including the place of discontinuity. The work done by the fluid as it emerges with volume v_2 against the pressure p_2 is

* 'Journal de l'École Polytechnique,' 1887, 1889.

† Compare Lamb's 'Hydrodynamics,' 1906, § 280.

$p_2 v_2$. On the whole, therefore, the external work done by the passage of the unit of mass is $p_2 v_2 - p_1 v_1$. The increase of kinetic energy of the fluid is

$$\frac{1}{2} (u_2^2 - u_1^2) = \frac{1}{2} m^2 (v_2^2 - v_1^2) = \frac{1}{2} (v_2 + v_1) (p_1 - p_2),$$

in virtue of (50), which requires that

$$p_1 - p_2 + m^2 (v_1 - v_2) = 0. \quad (81)$$

The sum of these is

$$p_2 v_2 - p_1 v_1 + \frac{1}{2} (p_1 - p_2) (v_2 + v_1) = \frac{1}{2} (v_2 - v_1) (p_2 + p_1). \quad (82)$$

We have next to consider the internal energy of unit of mass in the initial and final states. For this purpose we suppose the gas to expand adiabatically from its actual volume v to an infinite volume. In this expansion the work done by the gas is

$$\int_v^\infty p dv = \frac{pv}{\gamma - 1}, \quad (83)$$

so that the difference of internal energy in the two states is

$$\frac{p_2 v_2}{\gamma - 1} - \frac{p_1 v_1}{\gamma - 1}. \quad (84)$$

The principle of energy requires that the sum of this and (82) be zero, whence

$$\gamma = \frac{(p_2 - p_1)(v_1 + v_2)}{(p_1 + p_2)(v_1 - v_2)} \quad (85)$$

is the relation between the pressures and volumes in the two states. The result thus found by Hugoniot is the same as Rankine's. From Rankine's equation (65)

$$p_1 + m^2 v_1 = p_2 + m^2 v_2 = \frac{1}{2} (\gamma + 1) (p_1 + p_2) = \frac{1}{2} (p_1 + p_2) + \frac{1}{2} m^2 (v_1 + v_2),$$

it follows that

$$m^2 = \gamma \frac{p_1 + p_2}{v_1 + v_2} = \frac{p_2 - p_1}{v_1 - v_2}, \quad (86)$$

which is identical with (85).

The first remark that I will make is that, although Hugoniot assumes that the transition between the two states is sudden, there is nothing in his argument which requires this, all that is really necessary being that the *régime* is permanent. The next remark is that, however valid (85) may be, its fulfilment does not secure that the wave so defined is possible. As a matter of fact, a whole class of such waves is certainly impossible, and I would maintain, further, that a wave of the kind is never possible under the conditions, laid down by Hugoniot, of no viscosity or heat-conduction.

A closer examination of the process by which (85) was obtained will show that while the first law of thermodynamics has been observed, the second law has been disregarded. The crux of the matter lies in the comparison

of the internal energies of the incoming and outgoing gas expressed in (84). If (p_2, v_2) and (p_1, v_1) lie upon the same adiabetic, the work corresponding to the passage from the one state to the other is given without ambiguity by (84). But in the present case the two states do not lie upon the same adiabetic, and the work required is deduced upon the assumption that nothing is involved in the passage at $v = \infty$ from one adiabetic to the other. What is actually there required is the communication (positive or negative) of an infinitesimal quantity of heat. From the point of view of the first law the infinitesimal quantity of heat may be neglected, but not so from the point of view of the second law, since the transfer is supposed to take place at the zero of temperature. When heat and work are distinguished, infinitesimal heat at zero may have a finite value. The imaginary passage to infinity has the advantage of leading rapidly to the required conclusion, but it rather tends to obscure the real nature of the process. While all the other items of the account are mechanical work, the passage from one adiabetic to the other (which may take place at constant finite volume) is a question of *heat* as distinguished from work. If during a complete cycle work would be lost and corresponding heat gained, the operation is dissipative and there need be no contradiction if viscosity or heat-conduction enter, but the opposite contingency of a gain of work at the expense of heat is excluded in all cases. The conclusion is the same as before. While a wave of condensation may, perhaps, maintain a permanent regime as the result of dissipative agencies, a permanent wave of rarefaction is excluded.

It is remarked by Hugoniot that even when the ratio p_1/p_2 is infinite, v_2/v_1 does not exceed $(\gamma+1)/(\gamma-1)$, which for common gases is equal to about 6. A similar remark is made by Duhem,* who discusses the whole question with great generality. With regard to perfect gases "lorsqu'une quasi-onde de choc se propage au sein d'un gas parfait, le fluide le plus condensé est toujours en amont de l'onde et le fluide le moins condensé en aval." But, so far as I see, neither of these authors proves that the propagation is possible in any case.

It is a question of great interest to inquire what is the influence of viscosity and especially whether alone, or in co-operation with heat-conduction, it allows a wave of condensation to acquire a permanent regime. We proceed to consider this question on the basis of the usual equations, although it must be admitted that their application to conditions which are somewhat extreme raises points of uncertainty.

Reverting to our original equations, we recognise that (45) is unaffected

* 'Zeitschrift f. Physik. Chem.,' 1909, vol. 69, p. 169.

by the inclusion of viscosity, and that the change required in (46) is represented by writing*

$$X = \frac{4}{3\rho} \frac{d}{dx} \left(\mu \frac{du}{dx} \right),$$

so that (46) takes the form

$$m \frac{du}{dx} + \frac{dp}{dx} - \frac{4}{3} \frac{d}{dx} \left(\mu \frac{du}{dx} \right) = 0,$$

whence ($v = 1/\rho$)

$$p + m^2 v - \frac{4}{3} m \mu \frac{dv}{dx} = p_1 + m^2 v_1 = p_2 + m^2 v_2, \quad (87)$$

the terminal states (p_1, v_1) , (p_2, v_2) , being of uniformity, so that dv/dx there vanishes. From this it appears that (81), relating to the terminal states, holds good equally when viscosity is regarded.

A simple example under the head of viscosity is to suppose the temperature maintained uniform, as by a powerful radiation, so that the gas follows Boyle's law, making

$$pv = p_1 v_1 = p_2 v_2 = a^2.$$

From this and (87) we get

$$m^2 v_1 v_2 = a^2,$$

and

$$p_1 + m^2 v_1 = a^2/v_1 + a^2/v_2.$$

Using these in (87), we find

$$\frac{3m dx}{4\mu} = - \frac{v dv}{(v_1 - v)(v - v_2)}, \quad (88)$$

as governing the distribution of v along the line of propagation. In a wave of condensation $v_1 > v > v_2$, so that the denominator on the right of (88) is positive. Thus when m is positive, dv/dx is negative, as should be the case. On integration (μ constant)

$$\frac{3mx}{4\mu} = \frac{1}{v_1 - v_2} \{v_1 \log(v_1 - v) - v_2 \log(v - v_2)\}, \quad (89)$$

the origin of x being chosen suitably.

The transition of volumes from v_1 to v_2 occupies, mathematically speaking, the whole range from $x = -\infty$ to $x = +\infty$, but practically it may be very sudden. Since in (88) dx/dv never changes sign, the condition of permanency for a condensational wave can always be satisfied, whatever may be the value of the ratio v_1/v_2 † or p_1/p_2 , contrasting in this respect with the limitation found to be necessary on Rankine's conclusion relative to heat-conduction.

* Lamb's 'Hydrodynamics,' §§ 314, 316.

† But the limitation pointed out by Hugoniot still obtains; otherwise, one of the pressures would be negative.

As regards the velocity of wave propagation into the rarer medium, we have for its square

$$u_1^2 = m^2 v_1^2 = a^2 v_1 / v_2. \quad (90)$$

Returning to the case where heat development and viscosity are both regarded, we see that in virtue of (81) Hugoniot's reasoning is still applicable without change, and it leads to the same final relation (85) as was found by Rankine when heat-conduction is alone considered.

In endeavouring to apply Rankine's method to the more general case where viscosity is retained, we shall find it more convenient to treat v , or $(1/\rho)$, rather than p , as independent variable. If, as before, dQ denotes the total quantity of heat received by unit mass of the gas, we have from (60), (62),

$$(\gamma-1) \frac{dQ}{dx} = \gamma p \frac{dv}{dx} + v \frac{dp}{dx};$$

or, on elimination of p by means of (87),

$$(\gamma-1) \frac{dQ}{dx} = \gamma \left\{ p_1 + m^2 v_1 - m^2 v + \frac{4}{3} m \mu \frac{dv}{dx} \right\} \frac{dv}{dx} + v \left\{ -m^2 \frac{dv}{dx} + \frac{4}{3} m \frac{d}{dx} \left(\mu \frac{dv}{dx} \right) \right\}. \quad (91)$$

In (91) dQ consists of two parts, the first (dQ_1), with which alone Rankine dealt, the heat received by conduction, and the second (dQ_2) the heat developed internally under viscosity. As regards the latter, the heat developed in volume v and time dt is $\frac{4}{3} v \mu (du/dx)^2 dt$,* in which we are to replace dt by dx/u , and u by mv , so that

$$\frac{dQ_2}{dx} = \frac{4}{3} m \mu \left(\frac{dv}{dx} \right)^2. \quad (92)$$

Multiplying this by $(\gamma-1)$ and subtracting it from (91), we get

$$(\gamma-1) \frac{dQ_1}{dx} = \gamma (p_1 + m^2 v_1) \frac{dv}{dx} - (\gamma+1) m^2 v \frac{dv}{dx} + \frac{4}{3} m \frac{d}{dx} \left(\mu v \frac{dv}{dx} \right). \quad (93)$$

As in Rankine's investigation, the whole heat received by conduction in passing from one uniform state v_1 to another uniform state v_2 must vanish. Hence, on integrating between these limits, and dividing out the factor $(v_2 - v_1)$, we have

$$\begin{aligned} (\gamma+1) m^2 (v_1 + v_2) &= 2\gamma (p_1 + m^2 v_1) = 2\gamma (p_2 + m^2 v_2) \\ &= \gamma (p_1 + p_2) + \gamma m^2 (v_1 + v_2), \end{aligned}$$

or, as in (86),

$$m^2 (v_1 + v_2) = \gamma (p_1 + p_2),$$

the same relation as was found by Rankine. Introducing it into (93), we get

$$(\gamma-1) \frac{dQ_1}{dx} = \frac{1}{2} (\gamma+1) m^2 \left\{ (v_1 + v_2) \frac{dv}{dx} - \frac{dv^2}{dx} \right\} + \frac{4}{3} m \frac{d}{dx} \left(\mu v \frac{dv}{dx} \right). \quad (94)$$

* Lamb's 'Hydrodynamics,' § 341.

A particular case arises when we suppose the conductivity to be zero, so that dQ_1/dx vanishes throughout. We have then

$$\frac{4}{3}\mu v \frac{dv}{dx} + \frac{1}{2}(\gamma+1)m(v_1-v)(v-v_2) = 0, \quad (95)$$

differing from (88) only by the factor $\frac{1}{2}(\gamma+1)$. On the supposition that μ is constant, the solution is nearly the same as in (89), and, in fact, reduces to it when $\gamma = 1$, which represents Boyle's law. This case of no conduction is thus satisfactorily disposed of. Whatever be the ratio of pressures, a wave of condensation is always possible.

It should be remarked, however, that the supposition of constant μ does consist with the facts as known for actual gases when γ differs from unity. For such gases viscosity, though independent of *density*, varies with *temperature*, so that μ will not be constant in (95). But since μ is always positive, this complication merely affects the particular form of the integral and not the general conclusion as to the possibility of a permanent wave.

In general, from (94), if we reckon Q_1 from the terminal state v_1 ,

$$(\gamma-1)Q_1 = \frac{1}{2}(\gamma+1)m^2(v_1-v)(v-v_2) + \frac{4}{3}m\mu v \frac{dv}{dx}. \quad (96)$$

The equation of conduction is the same (74) as before. And for θ , from (87),

$$\theta = \frac{pv}{R} = \frac{v}{R} \left\{ \frac{\gamma+1}{2\gamma} m^2(v_1+v_2) - m^2v + \frac{4}{3}m\mu \frac{dv}{dx} \right\};$$

so that with regard to (62) the equation of conduction becomes

$$\begin{aligned} \frac{k}{mc} \left[m \frac{dv}{dx} \left\{ \frac{\gamma+1}{2\gamma} (v_1+v_2) - 2v \right\} + \frac{4}{3} \frac{d}{dx} \left(\mu v \frac{dv}{dx} \right) \right] \\ = \frac{1}{2}(\gamma+1)m(v_1-v)(v-v_2) + \frac{4}{3}\mu v \frac{dv}{dx}. \end{aligned} \quad (97)$$

By omitting the terms containing μ we may of course fall back on Rankine's problem.

Equation (97), in its general form, is much more complicated than when either viscosity or heat-conduction is alone regarded, in consequence of the occurrence of the differential coefficient of the second order. In general, both k and μ are functions of temperature, and therefore of v ; but, according to Maxwell's theory, which assumes a molecular repulsion inversely as the fifth power of the distance, $c\mu/k$ is independent of temperature (as well as of density), and takes the value $\frac{2}{3}$. And it would seem that this independence of temperature and density is general, seeing that the ratio is of no dimensions, at least so long as the repulsive force can be represented by an inverse power of the distance.* We shall write h for the above ratio and

* Compare 'Roy. Soc. Proc.,' 1900, vol. 66, p. 68; 'Scientific Papers,' vol. 4, p. 453.

assume that for a given gas it is an absolute constant. Thus, μ' being written for μ/m , (97) takes the form—

$$\mu' \frac{d}{dx} \left(\mu' \frac{dv^2}{dx} \right) + \mu' \frac{dv^2}{dx} \left\{ \frac{3(\gamma+1)}{8\gamma} \frac{v_1+v_2}{v} - \frac{3}{2} - h \right\} = \frac{3}{2} h (\gamma+1) (v_1-v)(v-v_2); \quad (98)$$

in which v^2 may be regarded as the dependent variable. For v^2 we shall write ξ , and if

$$U = \mu' d\xi/dx, \quad (99)$$

our equation, since it contains x only through dx , may be reduced to one of the first order in U and ξ , i.e.,

$$U \frac{dU}{d\xi} + U f(\xi) = F(\xi), \quad (100)$$

where
$$f(\xi) = \frac{3(\gamma+1)}{8\gamma} \frac{\sqrt{\xi_1} + \sqrt{\xi_2}}{\sqrt{\xi}} - \frac{3}{2} - h, \quad (101)$$

and
$$F(\xi) = \frac{3}{2} h (\gamma+1) (\sqrt{\xi_1} - \sqrt{\xi})(\sqrt{\xi} - \sqrt{\xi_2}). \quad (102)$$

If U can be found as a function of ξ from (100), x follows by simple integration of (99).

In considering equation (100) we may conveniently regard ξ as the linear co-ordinate of a material particle of unit mass moving in a straight line with velocity U . The first term, $U dU/d\xi$, then represents the acceleration of the particle; the second, $U f(\xi)$, may be regarded as a *resistance*, proportional to the velocity, and at the same time variable with the position (ξ); and the third term on the right hand represents a force, which is also a function of position. If t be the time in this subsidiary problem, $U = d\xi/dt$, and (100) may be written

$$\frac{d^2\xi}{dt^2} + f(\xi) \frac{d\xi}{dt} = F(\xi), \quad (103)$$

while by (99)
$$dx = \mu' dt. \quad (104)$$

If μ' be constant, the substitution of $\mu' t$ for x in (98) is obvious.

If we take $h = 0.4$, $\gamma = 1.41$, (101), (102), become

$$f(\xi) = 0.641 \frac{\sqrt{\xi_1} + \sqrt{\xi_2}}{\sqrt{\xi}} - 1.900, \quad (105)$$

$$F(\xi) = 0.723 (\sqrt{\xi_1} - \sqrt{\xi})(\sqrt{\xi} - \sqrt{\xi_2}). \quad (106)$$

It will be observed that, over the range from ξ_1 to ξ_2 , $F(\xi)$ is positive, but that the sign of $f(\xi)$ is doubtful. If ξ has the greater terminal value ξ_1 , f is negative; but, when it has the smaller terminal value ξ_2 , the sign depends upon the ratio ξ_1/ξ_2 . If this ratio < 1.21 , f is negative; otherwise it is positive.

I suppose that a complete analytical solution of our equation is not to be expected, and it is, indeed, hardly necessary for our purpose. What we most wish to know is whether a solution is possible which satisfies the prescribed conditions. Among these is the requirement that U in (100) vanish at both limits; and even then the manner of evanescence must be such as to secure that x , as determined by (99), shall be infinite at these limits. As the problem originally presents itself, we should have the representative particle travelling in the negative direction from ξ_1 to ξ_2 , starting with no velocity and arriving with no velocity. It seems simpler to consider it in a modified form, *i.e.* with the motion reversed, so that it takes place in the direction of the force F . There is, then, no question of the particle stopping between the limits and returning upon its course. We may make this change, if in (105) we reverse the sign of f . We consider, then, the motion of the particle to be in the positive direction, from ξ_2 to ξ_1 , with zero velocity at both limits, the motion between ξ_2 and ξ_1 being aided by the force F , which itself vanishes at these limits, and being also subject to a force of the nature of resistance, proportional to velocity. When ξ_1/ξ_2 does not exceed 1.21, the force is a resistance in the ordinary sense, *i.e.* it opposes the motion, and, in any case, it has this character near (and beyond) the arrival end ξ_1 . But when ξ_1/ξ_2 exceeds 1.21, the force becomes what we may call a counter-resistance, and aids the motion near the initial end ξ_2 . As regards F , in the neighbourhood of each limit it becomes a force proportional to distance therefrom, repulsive near ξ_1 , and attractive near ξ_2 . Thus, when ξ is nearly equal to ξ_2 ,

$$F(\xi) = 0.723 \frac{\sqrt{\xi_1} - \sqrt{\xi_2}}{2\sqrt{\xi_2}} (\xi - \xi_2); \quad (107)$$

and when ξ is nearly equal to ξ_1 ,

$$F(\xi) = 0.723 \frac{\sqrt{\xi_1} - \sqrt{\xi_2}}{2\sqrt{\xi_1}} (\xi_1 - \xi). \quad (108)$$

The particle, starting from ξ_2 , is bound to go through to ξ_1 . If it arrives at ξ_1 with zero velocity, we shall have, presumably, a solution of our problem. It is possible, however, that on first arrival at ξ_1 , it may pass through, and only settle down after a number of oscillations. To this there does not appear to be any objection; but if on the return from ξ_1 it overshoots ξ_2 , it can never again return to ξ_1 , since on the left of ξ_2 the sign of f is negative; and then our problem has no solution. On the other hand, from the nature of F , it is not possible for the particle passing through ξ_1 in the positive direction to escape returning.

The character of the start from ξ_2 can be investigated with the aid of approximate equations. Thus, in (100) we may treat $f(\xi)$ as constant, say

2α , where α may be either positive or negative, and take, as in (107), $F(\xi) = \beta(\xi - \xi_2)$, where β is positive, so that

$$U \frac{dU}{d\xi} + 2\alpha U - \beta(\xi - \xi_2) = 0. \quad (109)$$

If in (109) we assume

$$U = \lambda(\xi - \xi_2), \quad (110)$$

we find that the equation is satisfied provided that

$$\lambda = -\alpha \pm \sqrt{(\alpha^2 + \beta)}, \quad (111)$$

one value (λ_1) being positive and one (λ_2) negative. In the present case, where U must be positive when $\xi > \xi_2$, λ_1 is to be chosen.

The differential equation (109) can be made homogeneous, and its general solution,* when λ is real, can be put into the form

$$\frac{\{U - \lambda_1(\xi - \xi_2)\}^{\lambda_1}}{\{U - \lambda_2(\xi - \xi_2)\}^{\lambda_2}} = C, \quad (112)$$

when C is an arbitrary constant. This solution, of course, covers the cases where the particle starts from ξ_2 with a finite velocity (U_0), and it appears that $C = U_0^{\lambda_1 - \lambda_2}$. We might conclude from this that when $U_0 = 0$, then $C = 0$, but the conclusion is not safe. If, however, U and $\xi - \xi_2$ are of the same order of magnitude, we may write $U = r(\xi - \xi_2)$, where r is not infinite. Substituting this in (112), we get

$$(r - \lambda_1)^{\lambda_1} \cdot (r - \lambda_2)^{-\lambda_2} \cdot (\xi - \xi_2)^{\lambda_1 - \lambda_2} = C. \quad (113)$$

When $\xi - \xi_2$ vanishes, the third factor on the left is zero, and, since the first and second factors are not infinite, the conclusion follows that $C = 0$. This takes us back to (110), (111), the second solution (involving λ_2) relating to the case where U is negative, the motion being one of *approach* from the positive side to ξ_2 .

These conclusions may be arrived at more easily from (103), of which the general solution in the present case is

$$\xi - \xi_2 = A e^{\lambda_1 t} + B e^{\lambda_2 t}, \quad (114)$$

giving

$$U = \lambda_1 A e^{\lambda_1 t} + \lambda_2 B e^{\lambda_2 t}.$$

From these we may deduce

$$\begin{aligned} U - \lambda_1(\xi - \xi_2) &= (\lambda_2 - \lambda_1) B e^{\lambda_2 t}, \\ U - \lambda_2(\xi - \xi_2) &= (\lambda_1 - \lambda_2) A e^{\lambda_1 t}; \end{aligned} \quad (115)$$

whence (112) follows by elimination of t . For our present purpose, $\xi - \xi_2$ is to vanish when $t = -\infty$, so that $B = 0$; and (110) follows with $\lambda = \lambda_1$. It will be remarked that (110) makes x , as determined by (99), infinite when

* See, for example, Boole's 'Differential Equations,' p. 33.

$\xi = \xi_2$. The circumstances of the start from ξ_2 are thus definite and suitable. The question is as to the arrival at ξ_1 .

In the neighbourhood of ξ_1 the approximate equation is

$$U \frac{dU}{d\xi} + 2\alpha'U - \beta'(\xi - \xi_1) = 0, \quad (116)$$

where α' is positive and, by (108), β' negative. If now

$$U = \lambda'(\xi - \xi_1), \quad (117)$$

the values of λ' are $\lambda' = -\alpha' \pm \sqrt{(\alpha'^2 + \beta')}$; (118)

so that both values, if real, are negative. On the supposition of reality, (112) retains its form (with ξ_1 for ξ_2). If the velocity of arrival (U_0) be finite, $C = U_0^{\lambda'_1 - \lambda'_2}$, as before; and it might be supposed that, if U_0 vanishes when $\xi - \xi_1 = 0$, C would have to vanish or become infinite. Such a conclusion would be incorrect. If in (113) we suppose λ'_1 to be numerically the smaller of the two values, the third factor indeed vanishes with $(\xi - \xi_1)$ as before; but the conclusion that $C = 0$ is evaded if ultimately $r = \lambda'_1$.

The situation is most easily understood from the solution in terms of t as in (114), (115). Since λ'_1, λ'_2 are *both* negative, the condition that $\xi - \xi_1$ and U shall vanish together when $t = \infty$ is satisfied, whatever may be the values of A and B . There are now an infinite number of possible types of solution, instead of only one as in the former case. And it appears that the two simple types included under (117) are not at all upon an equal footing. Except in the *particular* case where $A = 0$, the solution always tends ultimately to the form $U = \lambda_1(\xi - \xi_1)$, and of course it may assume this form throughout. All these solutions satisfy the condition as to the infinitude of x when $U = 0$.

Whether the values of λ' be real or not, the particle must ultimately settle down at ξ_1 , unless it escape from the region to which the approximate equation applies. For in (118) the *real part* of λ' is always negative.

Returning to (100) in its general form, let us consider the variation of U for a given ξ as dependent upon variations in f and F . We have

$$U \frac{d\delta U}{d\xi} + \delta U \frac{dU}{d\xi} + f \cdot \delta U + U \cdot \delta f - \delta F = 0,$$

or
$$\frac{d\delta U}{d\xi} + P\delta U - Q = 0, \quad (119)$$

where P and Q are supposed to be known functions of ξ , viz.,

$$P = \frac{f + dU/d\xi}{U}, \quad Q = \frac{\delta F - U \cdot \delta f}{U}. \quad (120)$$

The solution of the linear equation (119) is

$$\delta U = e^{-\int P d\xi} \left(\int e^{\int P d\xi} Q d\xi + c \right). \quad (121)$$

If $Q = 0$, δU has the same sign as c , so that an increment of velocity communicated at any point remains throughout of the same sign. Again, if Q be throughout of one sign, δU , as dependent upon it, has the same sign. For example, if U be positive over the range considered, δf positive, and δF negative, then δU is certainly negative. The increments δf , δF may be local, vanishing over any part of the range.

The application to the present problem is obvious. If the particle passing any point between ξ_2 and ξ_1 , with velocity U , arrives at ξ_1 for the first time without velocity, it will still arrive at ξ_1 without velocity (it must in any case arrive, since F is positive), if U be diminished, or if f be increased, or if F be diminished, or if all these changes occur together. And in the limit, when ξ_1 is closely approached, the ratio of U to $(\xi_1 - \xi)$ is in general the same.

By use of this principle we may assure ourselves as to the possibility of a solution in certain cases where ξ_1/ξ_2 does not greatly exceed unity. We imagine a simplified problem which admits of analytical solution and is derived from the actual one by alterations which everywhere (over the range from ξ_2 to ξ_1) increase F and diminish f . If this modified problem admits of the solution required, *a fortiori* will the original problem do so.

If we consider the curve which according to (106) represents F as a function of ξ , we see that it is concave downwards, and that F will everywhere be increased if we substitute for the curve the two terminal tangents at ξ_2 and ξ_1 , whose equations are given in (107), (108). The abscissa of K , the point of intersection, is $\xi = \sqrt{(\xi_2 \xi_1)}$. (Fig. 1.)

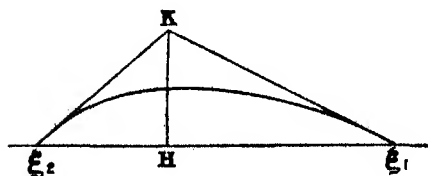


FIG. 1.

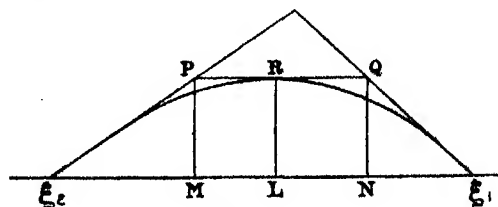


FIG. 2.

As regards f , its value is given by (105) with sign reversed, and is diminished when ξ is diminished. The changes will therefore be in the required direction if we represent f over $\xi_2 H$ by its value at ξ_2 , viz.,

$$f_2 = 2\alpha = 1.259 - 0.641s, \quad (122)$$

and from H to ξ_1 by its value at H , viz.,

$$f_1 = 2\alpha' = 1.900 - 0.641(s^2 + s^{-2}), \quad (123)$$

if for brevity we write s for $\sqrt{(\xi_1/\xi_2)}$, so that s is the ratio of terminal densities in the original problem.

As regards the first portion of the course, the solution already given (110), (111), determines the value of U on arrival at H . We have

$$U = \lambda_1 \xi_2 (s-1), \quad \text{where} \quad \lambda_1 = \sqrt{(\alpha^2 + \beta) - \alpha},$$

in which α is given by (122) while by (107) $\beta = 0.361(s-1)$. Using these, we get

$$U = (s-1) \xi_2 [\sqrt{\{(0.630 - 0.320s)^2 + 0.361(s-1)\}} - 0.630 + 0.320s]. \quad (124)$$

If $s = 1 + \sigma$, where σ is small, (124) becomes

$$U = \sigma \xi_2 \times \frac{\beta}{2\alpha} = 0.584 \xi_2 \sigma^2. \quad (125)$$

As regards the second portion of the course, the appropriate solution is provided by (117), (118), where λ' is restricted to be real. And in accordance with our suppositions α' is given by (123) while from (108) $\beta' = -0.361(1-s^{-1})$. In choosing between the values of λ' we are at liberty to take that which gives the largest value of U at H consistent with $U = 0$ at ξ_1 , viz.,

$$\lambda'_2 = -\alpha' - \sqrt{(\alpha'^2 + \beta')}.$$

$$\text{Thus at } H \quad U = (s^2 - s) \xi_2 \{\alpha' + \sqrt{(\alpha'^2 + \beta')}\}, \quad (126)$$

or approximately, in terms of σ (supposed small),

$$U = \sigma \xi_2 (0.618 + 0.033\sigma). \quad (127)$$

From (125), (127) we may infer that when σ is small, i.e. when s does not much exceed unity, the particle, starting from ξ_2 , arrives at H with a velocity small enough to admit of its being stopped on arrival at ξ_1 , even under the simplifying conditions that have been imposed, and therefore *a fortiori* under the actual conditions of the problem. Hence when ξ_1 does not too much exceed ξ_2 , a wave of permanent regime is possible as the result of viscosity and heat-conduction.

But the range of ξ_1/ξ_2 thus proved admissible is rather severely limited. The postulated reality of λ' requires that $\alpha'^2 + \beta'$ be positive, and this again requires that $s < 1.34$. For values of s greater than this the motion in the simplified problem would become oscillatory. Calculation shows that, for $s = 1.34$, (124) gives

$$U = (s-1) \xi_2 \times 0.20,$$

while (126) gives

$$U = (s-1) \xi_2 \times 0.43;$$

so that up to this limit the particle starting from ξ_2 in the simplified problem, and therefore also in the actual problem, would arrive at ξ_1 with zero velocity. Up to a ratio of densities equal to 1.34, the wave of permanent regime is certainly possible.

The next step in this line of procedure will be to replace the curve

representing F by the broken line $\xi_2 PQ \xi_1$ formed by *three* of its tangents, of which two are the same terminal tangents as before, while the third, PQ , may be taken to be the horizontal tangent parallel to $\xi_1 \xi_2$. (Fig. 2.) By (106) the point L where F is a maximum is determined by

$$\sqrt{\xi} = \frac{1}{2}(\sqrt{\xi_1} + \sqrt{\xi_2}) = \frac{1}{2}\sqrt{\xi_2}(s+1),$$

and the corresponding value of F is

$$0.1875 \xi_2 (s-1)^2.$$

The abscissæ of the points of intersection of the horizontal tangent with the terminal tangents are given by (107), (108). For M

$$\xi = \frac{1}{2}\xi_2(s+1),$$

and for N

$$\xi = \frac{1}{2}\xi_2(s^2+s).$$

As for f we are to take along $\xi_2 M$ the value at ξ_2 ; along MN the value at M ; and along $N \xi_1$ the value at N , as given by (105), with sign changed.

For the two terminal portions the solutions are of the same form as before, but for the middle portion a new form is required. Making F constant in (100) and writing $2\alpha''$ for f , we find on integration

$$-4\alpha''^2 \xi = F \log(F - 2\alpha''U) + 2\alpha''U + C, \quad (128)$$

where C is an arbitrary constant, to be determined so as to suit the velocity with which the particle arrives at M .

As before, the limiting value of s is determined by the consideration that, for our purpose, the arrival at ξ_1 must not be oscillatory. We get $s = 1.633$ about, and with this value of s it is not difficult to show that the velocity of arrival at N is below the value prescribed by the solution for $N \xi_1$. The necessary conditions are thus fulfilled and we infer that the wave of uniform regime is possible so long as $s < 1.63$. Although this ratio is moderate, it exceeds that found admissible in Rankine's problem, which leaves viscosity out of account. We there found that the greatest admissible ratio of *pressures* was 1.61, which by (68) corresponds to 1.40 for the ratio of *densities*. Of course, in Rankine's problem the solution definitely fails at this point, while in the present problem all that we have so far proved is that the limit exceeds 1.63.

From the low limiting values of s found necessary in these two cases in order to secure the reality of the roots of (118), it might be inferred that the reality would fail for the limiting motion in the neighbourhood of ξ_1 , when s had a considerable value, but such is not the case. If we use the value of f from (105) appropriate to the terminal point ξ_1 itself, we have

$$2\alpha' = 1.900 - 0.641(1+s^{-1}) = 1.259 - 0.641s^{-1};$$

and

$$\beta' = -0.3615(1-s^{-1}).$$

Thus, even when $s = \infty$,

$$\alpha'^2 + \beta' = 0.3963 - 0.3615 = +0.0048;$$

and the roots are always real. Hence, subsidence at ξ_1 is not ultimately oscillatory, but there is nothing in this argument to exclude a finite number of oscillations before subsidence into the region governed by the approximate equation.

The method of approximation already followed might be pushed further, but it seems preferable to use the general method of numerical calculation for the solution of differential equations as formulated by Runge.* The equation is that numbered (100), in which f (whose sign is to be reversed) and F are given by (105), (106). If we write $U' = U/\xi_2$, $\xi' = \xi/\xi_2$, our equation takes the form

$$\frac{dU'}{d\xi'} = \frac{0.723}{U'}(s - \sqrt{\xi'})(\sqrt{\xi'} - 1) - 1.900 + \frac{0.641(1+s)}{\sqrt{\xi'}}. \quad (129)$$

The value of s being given, it is required to trace the connection between U' and ξ' , simultaneous values being denoted respectively by a and b . If a receive the increment h , we have to calculate the corresponding increment k for b . If we call the function on the right of (129) $\phi(\xi', U')$, Runge gives as a first approximation to k

$$k_1 = \phi(a + \frac{1}{2}h, b + \frac{1}{2}\phi_0.h)h, \quad (130)$$

where $\phi_0 = \phi(a, b)$. The next approximation is

$$k = k_1 + \frac{1}{3}(k_2 - k_1), \quad (131)$$

where $k_2 = \frac{1}{2}(k' + k'')$ and $k' = \phi_0.h$,

$$k'' = \phi(a + h, b + k')h, \quad k''' = \phi(a + h, b + k'')h. \quad (132)$$

Having determined the new simultaneous values $a + h$, $b + k$, we make a fresh departure therefrom, and so trace out the function step by step.

In the present application the starting point is $a = 1$ (i.e. $\xi = \xi_2$), $b = 0$, and we have to trace the function until $\xi' = s^2$. The initial value of ϕ is to be found from (129) by putting $\xi' = 1$. Writing $U' = \phi_0(\xi' - 1)$, we get

$$\phi_0^2 + \{1.900 - 0.641(1+s)\}\phi_0 - \frac{1}{2} \times 0.723(s-1) = 0, \quad (133)$$

of which the positive root is to be chosen.

The extreme admissible value of s in our present problem is 6, and the first and rather elaborate calculation that I have made relates to this case. From (133) $\phi_0 = 3.1591$, so that taking $a = 1$, $b = 0$, $h = 1$, we have $k' = 3.1591$. Calculating from (130) we find $k_1 = 2.255$, and from (132)

$$k'' = 1.7076, \quad k''' = 2.0772,$$

* See Forsyth's 'Differential Equations,' p. 51.

making $k_2 = 2.6182$. Hence the correction to k_1 , viz., $\frac{1}{2}(k_2 - k_1)$, is equal to 0.121, and $k = 2.376$. Thus, corresponding to $\xi' = 2$, we get $U' = 2.376$. The following are the values of U' obtained successively in this way:—

ξ'	U'	ξ'	U'	ξ'	U'
1	0.000	14	7.502	33	1.2942
2	2.376	18	6.807	34	0.8632
3	3.903	22	5.674	35	0.4160
4	4.986	26	4.241	35½	0.2043
6	6.380	30	2.610	35¾	0.1012
10	7.526	32	1.736	36	0.0004

The correction to k_1 is everywhere subordinate. In the last step from $35\frac{3}{4}$ to 36 no correction to k_1 is applied.

There is a little difficulty in tracing by this method and with full accuracy the final progress to zero when $\xi' = 36$. If any doubt be left, it may be removed by applying the former method to the course from 35 to 36, using the value of f appropriate to 35 and the terminal tangent as the representative of the curve for F . From this it appears that even if U' at $\xi' = 35$ were as great as 0.7468, the moving particle could not pass $\xi' = 36$. The conclusion is that even in this extreme case of $s = 6$ the solution exists, and that a wave of permanent regime is possible. Further, from (99) we see that since U and μ' are both positive, $d\xi/dx$ is positive throughout, and the transition from the one density to the other takes place *without alternation*.

After what has been proved little doubt could remain but that a solution is possible when s has any value lower than 6. I have, however, thought it desirable to add a rough calculation (rough on account of the relative magnitude of the steps) for the case of $s = 3$:—

ξ'	1	2	3	5	7	8	8½	9
U'	0.00	0.90	1.19	1.26	0.82	0.40	0.19	0.01

It is a question of some importance to consider what is the thickness of the transitional layer in the waves of uniform regime which have been proved to be possible. Mathematically speaking, the transition occupies an infinite space; but if we understand the expression to refer to a transition approximately complete, the thickness involved is finite, and indeed extremely small. Reference to (98) shows that x is of the order μ' , or μ/m , or $\mu/\rho u$, where u is the velocity of the wave. For the present purpose we

may take u as equal to the usual velocity of sound, *i.e.* 3×10^4 cm. per second. For air under ordinary conditions the value of μ/ρ in C.G.S. measure is 0.13; so that x is of the order $\frac{1}{3} \times 10^{-6}$ cm. That the transitional layer is in fact extremely thin is proved by such photographs as those of Boys, of the aerial wave of approximate discontinuity which advances in front of a modern rifle bullet; but that according to calculation this thickness should be well below the microscopic limit may well occasion surprise.

Resistance to Motion through Air at High Velocities.

According to the adiabatic law the pressures and velocities in a compressible fluid free from external force, see (47), are related by

$$\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = 1 + \frac{\gamma-1}{2} \frac{u_1^2 - u_2^2}{a_1^2}, \quad (134)$$

in which p_1, ρ_1, u_1 denote the pressure, density, and velocity at one point of the path; p_2, ρ_2, u_2 the corresponding quantities at another point. Also $a_1^2 = \gamma p_1/\rho_1$, so that a_1 is the velocity of infinitesimal disturbances in the condition (1). In an early paper* I suggested the application of this formula to bodies moving through air at high velocities. Regarding the obstacle as stationary and the fluid in motion with velocity u_1 and pressure p_1 , the pressure p_2 corresponding to the loss of this velocity is given by putting $u_2 = 0$ in (133), a_1 being the ordinary velocity of sound. This is the pressure which should obtain at the axial point on the nose of a symmetrical bullet, and although this value in strictness represents the *maximum* pressure, the analogy of an incompressible fluid suggests that the mean pressure on a flat surface would not be greatly inferior. But in a recent discussion,† Mr. Mallock has shown that this formula immensely overestimates the resistance actually experienced by a bullet, and (so far as I am aware) the discrepancy remains unexplained.

If indeed the adiabatic law really prevailed throughout, there could be no escape from the conclusion formulated. A consideration of the photographs by Boys‡ will suggest the required explanation. At a short constant distance in front of the bullet there is an aerial bore, or place of approximate discontinuity. Along the axis, the fluid moving up to the bullet changes its density, and therefore pressure and temperature, *suddenly*, so that there is here a special opportunity for viscosity and heat-conduction to take effect. The pressures and velocities on the two sides of the bore are

* 'Phil. Mag.' 1876, vol. 2, p. 430; 'Scientific Papers,' vol. 1, p. 289.

† 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 266.

‡ 'Nature,' 1893, vol. 47, p. 440. The particular photograph reproduced by Mallock does not exhibit well the feature in question.

related, not according to the adiabatic law, but according to Rankine's law already discussed. The changes which occur may be separated into two stages. The first is the sudden one in which the fluid passes from the atmospheric condition p_0, ρ_0 , with velocity u_0 to the condition denoted by p_1, ρ_1, u_1 . After passing the bore the fluid changes gradually according to the adiabatic law already stated until at the nose of the bullet the condition is represented by p_2, ρ_2 , with $u_2 = 0$.

We are now in a position to calculate the final pressure p_2 . For the first stage we have Rankine's formula (67), making

$$\rho_0 u_0^2 = \frac{1}{2}(\gamma - 1)p_0 + \frac{1}{2}(\gamma + 1)p_1,$$

or, if $\alpha^2 = \gamma p_0 / \rho_0$,

$$\frac{p_1}{p_0} = \frac{2\gamma}{\gamma + 1} \frac{u_0^2}{\alpha^2} - \frac{\gamma - 1}{\gamma + 1}, \quad (135)$$

determining the pressure just inside the bore in terms of u_0 (the velocity of the bullet through quiescent air) and α , the ordinary velocity of sound. When $u_0 = \alpha$, $p_1 = p_0$. For values of u_0 less than α , the first stage does not exist and we may suppose $p_1 = p_0$, $u_1 = u_0$.

In the second stage we use (134) with $u_2 = 0$. Thus

$$\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = 1 + \frac{\gamma-1}{2} \frac{\rho_1 u_1^2}{\gamma p_1}, \quad (136)$$

in which, by a formula analogous to (66),

$$\rho_1 u_1^2 = \frac{1}{2}(\gamma + 1)p_0 + \frac{1}{2}(\gamma - 1)p_1.$$

Hence

$$\left(\frac{p_2}{p_0}\right)^{\frac{\gamma-1}{\gamma}} = \frac{(\gamma + 1)^2}{4\gamma} \left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{\gamma}} \left\{ 1 + \frac{\gamma-1}{\gamma+1} \frac{p_0}{p_1} \right\}. \quad (137)$$

When $u_0 > \alpha$, p_1/p_0 is to be calculated from (135). When the resulting value is substituted in (137), p_2/p_0 is determined.

When $u_0 < \alpha$, we have simply

$$\left(\frac{p_2}{p_0}\right)^{\frac{\gamma-1}{\gamma}} = 1 + \frac{\gamma-1}{2} \frac{u_0^2}{\alpha^2}. \quad (138)$$

If u_0/α be *small*, (138) reduces to

$$\frac{p_2}{p_0} = 1 + \frac{\rho_0 u_0^2}{2p_0},$$

or

$$p_2 - p_0 = \frac{1}{2} \rho_0 u_0^2, \quad (139)$$

as for an incompressible fluid.

When $u_0 = \alpha$, both systems give

$$\left(\frac{p_2}{p_0}\right)^{\frac{\gamma-1}{\gamma}} = \frac{\gamma+1}{2}. \quad (140)$$

When u_0/a is large, the second terms on the right of (135) and (137) may be neglected, and we obtain

$$\frac{p_2}{p_0} = \frac{\gamma+1}{2} \frac{u_0^2}{a^2} \left\{ \frac{(\gamma+1)^2}{4\gamma} \right\}^{\frac{1}{\gamma-1}}; \quad (141)$$

or, when we put $\gamma = 1.41$,

$$p_2/p_0 = 1.30 u_0^2/a^2. \quad (142)$$

The following are some corresponding values of p_2/p_0 and u_0/a , calculated from (135), (137), with $\gamma = 1.41$:—

u_0/a	1	2	3	4
p_2/p_0	1.90	4.49	11.7	20.7

From this point onwards the approximate formula (142) may suffice. The values found are in good agreement with Mr. Mallock's curve.

The question as to the linear interval between the bore and the nose of the bullet cannot be answered from the results of the present paper. In strictly one-dimensional motion, the bore and the plane wall constituting the obstacle could not move at the same speed.

The Origin and Growth of Ripple-mark.

By Mrs. HERTHA AYRTON.

(Communicated by the late Prof. W. E. Ayrton, F.R.S. Received April 21, 1904; received in revised form May 26, 1904; read June 16, 1904.*)

[PLATES 3 AND 4.]

To any one who, for the first time, sees a great stretch of sandy shore covered with innumerable ridges and furrows, as if combed with a giant comb, a dozen questions must immediately present themselves. How do these ripples form? Are they made and wiped out with every tide, or do they take a long time to grow, and last for many tides? What is the relation between the ripples and the waves to which they owe their existence? And a host of others too numerous to mention.

The questions to which I particularly directed my attention at first were the following:—(1) How do the ripples first start? (2) What is the relation between the water waves and the ripples?

During the course of this investigation certain fresh facts have come to light, showing how the principles involved in the formation of ripple-mark apply to other phenomena of apparently widely different origin. Some of these are included in the present communication, but the discussion of others, less immediately connected with ripples, I have deferred to a future occasion.

1. *Starting of the First Ripple.*—To the first question as to the *origin* of ripple-mark—fundamental as it is—I could, for some time, find no satisfactory answer, either in nature or in books. Even the deeply interesting paper† in which Prof. George Darwin described the vortices he had discovered in the water oscillating over ripple-mark touched but lightly on this point. Prof. Darwin said: “When a small quantity of sand is sprinkled [in a glass trough] and the rocking begins, the sand dances backwards and forwards on the bottom, the grains rolling as they go.

“Very shortly the sand begins to aggregate into irregular little flocculent masses, the appearance being something like that of curdling milk. *The position of the masses is, I believe, solely determined by the friction of the sand on the bottom.*”

And again: “We now revert to the initiation of ripple-mark.

“If the surface be very even, as when sand is sprinkled on glass, when a uniform oscillation of considerable amplitude be established, the sand is

* [Publication postponed by author's desire until June, 1910.]

† “On the Formation of Ripple-mark in Sand,” ‘Roy. Soc. Proc.’ November 22, 1883, vol. 38, p. 23.

carried backwards and forwards and *some of the particles stick in places of greater friction. As soon as there is any superficial inequality*, it is probable that a vortex is set up in the lee of the inequality which tends to establish a dune there." [The italics are mine.]

With all the respect I felt for so eminent an observer—one, also, who had thrown so much light on the subject—I could not concur in this opinion. It seemed to me impossible that chance inequalities, having no relation with one another, but scattered here and there entirely without order, should develop into such ripples as are commonly seen on the sea shore—straight as if ruled, all of the same shape, and all at equal distances apart, or at distances varying according to some definite law. I cast about, therefore, for some other solution to the problem—some way of connecting the ripples with one another from the beginning, without the intervention of chance irregularities in the sand. I may say at once that I have been successful in finding such a solution, and that I am about to show how oscillating water can produce ripple-mark on sand which is perfectly smooth and level to start with, and free from irregularity of every sort.

My first experiments were carried out at Margate, with the rather coarse brown sand found there. I tried oscillating water of various depths, over different thicknesses of sand, in vessels of all sorts of shapes and sizes, from a soap dish some 4" x 3" x 2" to a tank 44" x 18" x 18". The oscillations were produced by giving the vessel either slight instantaneous horizontal pushes, or a very small rocking motion, in time with the natural swing of the water,* and by putting either rollers or cushions under the vessel to ease the jerks. The sand was made quite level at the beginning of each experiment, by being violently stirred up first, and then gently and irregularly shaken while it was settling.

In every vessel ripples appeared in times varying from a few seconds to a few minutes; and in all those in which the water was simply made to rise and fall alternately at each end of the vessel, without the formation of intermediate waves, two things invariably happened:—(1) Ripples formed first across the *middle* of the vessel, a fact first observed by C. de Candolle,† and (2) after prolonged oscillation most of the sand had collected there also in a long ripple-marked heap, as shown in fig. 1 (Plate 3).

Since ripples formed first across the middle of the vessel, and as, also, the sand was gradually removed from near the ends to the middle, by prolonged

* When each impulse is prolonged, even although the impulses be in time with the natural vibration of the water, the effect on the sand is quite different, for a reason that will be given in another paper.

† "Rides Formées à la Surface du Sable Déposé au Fond de l'Eau," 'Archives des Sciences Physiques et Naturelles,' Période 3, vol. 9, p. 253 (1883).

oscillation, it seemed clear that it was the formation of a small ridge* across the middle, during the first few oscillations, that caused the ripples to start there first.

In order both to reduce surface friction, and to render observation easy, I repeated the experiment, scattering a mere pinch of sand as evenly as possible over the smooth bottom of a pie dish, some 8 inches' long, containing about an inch of water. In this way, each grain, being isolated from the next, could be easily moved by the water, and as readily observed. The result was very striking. After oscillation of the water for less than half a minute, *the whole of the sand was collected in a straight line across the middle of the dish at right angles to the line of motion.*

Scattering the sand again, and watching carefully how the water moved it, I saw that each swing† of the water pushed every grain that was being swept *towards* the middle farther than the next swing carried it *away* again from the middle. If *a*, for instance (fig. 2), were the position of a grain at the

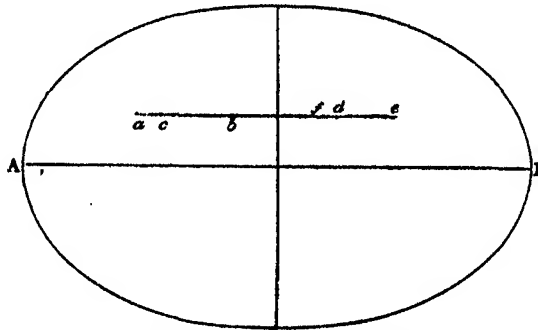


FIG. 2.—Change of Position of Sand Grains due to one Complete Oscillation of the Water.

beginning, and *b* its position at the end of a swing of the water from *A* to *B*, then when the water was going back from *B* to *A*, in the next swing, the grain would be swept to *c* only, so that the net result of one complete oscillation would be the removal of the grain from *a* to *c*, *i.e.*, *towards the middle*.

On the other side, during the same complete oscillation, a grain at *d* would have been swept by the first swing to *e*, and by the second, past *d* to *f*, so that this grain also would have been moved *towards the middle*. Finally, therefore one complete oscillation would have altered the distance between the grains from *a d* to *c f*. In this way all the grains very soon reached the middle line

* I use the word "ridge" to define an elevation, and a "ripple" to mean a ridge and furrow combined.

† I call each travel of the impulse from one end of the vessel to the other a "swing," so that there are two swings to each complete oscillation.

of the dish, and remained oscillating over it as long as the motion of the water was kept up.

It is clear that the formation first of the middle ripples, and the collecting of a mound across the middle of the vessel after prolonged oscillation could only be extensions of the operation just described. This, then, is the way in which the first ridge can form without the aid of any chance excrescence to start it.

When water is kept oscillating over sand, then, the dance of the grains described by Prof. Darwin is not, as he conjectured, a simple swaying to and fro, which would leave each grain where it found it, but for chance inequalities of the surface. *It is, on the contrary, a steady periodic advance from places where the horizontal velocity of the water is least to places where it is greatest, each oscillation leaving the grains nearer to their goal than it found them.*

Since water which rises and falls alternately at each end of a vessel, while its level remains nearly constant at the middle, is really oscillating in a stationary wave, of which the middle of the vessel is a loop, as regards horizontal motion, and the ends are nodes, it is interesting to note that the sand, in gathering across the middle of a vessel, is really collecting at a loop of the stationary wave generated by the oscillation of the water.*

2. *The Formation of Fresh Ripples beside an Existing One.*—Having established the primary ridge, and found the conditions necessary for its formation from smooth and level sand, the next question that arose was, how are all the other ripples started? Do they depend for their initiation simply on unevennesses of the surface, or are they also subject to some definite law? M. Forel† noted that a foreign body in the sand set up, in some way or other, a series of ripples in the sand on either side of it; but how these ripples start—whether all at one instant or each separately—and what is the process of initiation, has not, I think, hitherto been elucidated.

The solution of the problem cost me several weeks of observation and experiment, yet it was absurdly simple when it came. It was that a single ripple, existing alone, in otherwise smooth sand, initiates a ripple on

* The terms "loop" and "node" have a perfectly definite meaning when applied to a vibrating string, for example, and mean the places of maximum and minimum motion. But when applied to a fluid oscillating with stationary waves, the terms are apt to be misleading, since in the place where the vertical motion is practically zero the horizontal motion is a maximum, and where the horizontal motion is practically zero the vertical motion is a maximum. Hence the node for vertical motion is the loop for horizontal motion, and *vice versa*.

† 'Archives des Sciences Physiques et Naturelles,' Période 3, vol. 10, p. 39.

either side of it, that each of these ripples produces another on its farther side—these in their turn originate other ripples on their farther sides, and so on, till the whole sand is ripple-marked. This suggestion having occurred to me, I tried in many ways to make sure that it was correct. For instance, I formed a fairly high ridge at some distance from the middle of the vessel, and watched to see if others followed from that, before the primary ridge in the middle became visible; or, again, I made a ridge of some peculiar shape, such as this in plan, \rangle , and noted whether the succeeding ridges took the same, or nearly the same, shape; and they did, the angle in each one being more obtuse than in that formed before it. Thus I felt sure of the fact; it only remained to see how it was accomplished.

For this purpose I abandoned my brown sand in favour of silver sand, which I had found to be so mobile that it spun in delicate fairy-like vortices in the leas of some of the ridges. These vortices, which differed widely from those discovered and described by Prof. Darwin, were, as I afterwards

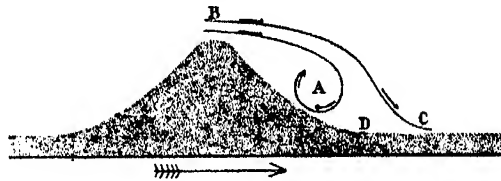


FIG. 3.—A Ripple-forming Vortex with Generating Ridge.

found, the true ripple-forming vortices, and I therefore call them ripple vortices.

3. *Structure and Functions of the Ripple Vortex.*—The vortices I saw had horizontal axes and were spiral in shape, and they seemed to scoop sand out from the bases of the ridges, and to push some of it up the ridges while they carried the remainder whirling round with them. In watching them it occurred to me that since each vortex (A, fig. 3) raised sand up the ridge against which it revolved, while the water that flowed over the vortex BC (fig. 3) swept sand away from that ridge, there must be some neutral line parallel to the ridge at about D (fig. 3), on one side of which sand was being swept in one direction and on the other side in the other; and that, if that were so, a hollow must be formed parallel to the ridge, and reaching to some little distance on either side of the neutral line. Such a hollow must, it seemed to me, form a new furrow, while the wall of it on the side remote from the ridge must ultimately become a new ridge.

In order to see if my surmise was correct, it was necessary to simplify and

magnify the action of the water, and also to see its stream lines. To simplify it I used only enough sand to cover the bottom of my glass trough ($36'' \times 6'' \times 8''$), and I got rid of sand on the ridge by making an artificial ridge of two china tiles sewn up in calico. To magnify the action, this ridge was made 2 inches high, and, so that no water should get round it or under it, it fitted tightly across the trough, and was jammed down on to the bottom.

Prof. Darwin employed ink squirted on to the sand to show him the stream lines of the water; but, as I found that this was impracticable with the violent motion necessary to raise sand vortices, I cast about to find an insoluble powder that had only a slightly greater specific gravity than water, so that it should move with the water in all its twists and turns. I found that well-soaked ground black pepper, after all the finest particles had been

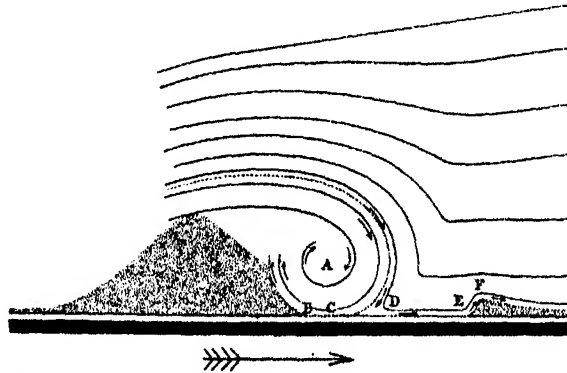


FIG. 4.—Ridge with Ripple Vortex, A; Neutral Line, D; and Brush, D E F.

washed away, answered my purpose perfectly. With this I was soon able to follow the exact course of the water under every kind of condition, and fig. 4 shows what happened during a swing from left to right when the artificial ridge was in position, and when about a dessertspoonful of pepper was in the water.

Soon after the water began to flow over the ridge a small vortex appeared on its right-hand side. As water continued to pour over the ridge the vortex enlarged, so that its centre moved farther away from the ridge; finally there was a large vortex as at A (fig. 4), with water flowing down outside it, some of which, when it reached the bottom, struck the sand there *towards* the ridge, as at B, while the outer portion swept sand *away* from the ridge, as at D and E, leaving a bare space, which was what I have called the neutral line, between C and E, with its centre at D. With the return swing in the opposite direction, the vortex, with its whirling sand, was

carried bodily over to some 3 inches on the other side of the ridge, the left side, where it dropped all the sand that had not fallen by the way. Then a similar vortex, a clear space, and a thickening of the sand to the left of it, appeared on the left-hand side of the ridge. These clear spaces were, of course, new furrows, and the sand walls farthest from the ridge were new ridges. After a few more oscillations not only did these grow into very decided ridges, but each of them had, in its turn, originated fresh furrows and ridges, and soon the whole of the space between the original ridge and both ends of the trough was covered with ripple-mark.

Since the water that strikes obliquely into the sand (DEF, fig. 4), after flowing over the vortex, clears a new furrow and sweeps up a new ridge exactly as a brush clears the floor and sweeps the dust up into a ridge, I shall call this water the "brush." The pepper, then, showed that the vortices and brushes cleared out new furrows and swept up fresh ridges exactly as I had imagined they did.

There are thus three ways in which sand ripples are originated, viz., the "uneven surface" method, the "differential motion" method, and the "brush" method. The first, which was the one described by Prof. Darwin, could, unaided, give rise to irregular ripple-mark only, since it consists in piling up sand in places where the surface chances to be uneven. The second is the method by which single ridges arise at the loops of stationary waves. The third is that by which the brush of the vortex in the lee of any existing dune or obstacle sweeps up a new ridge beside it, leaving a hollow along the neutral line of the vortex. The last two methods are evidently capable, unaided, of originating and then extending *regular* ripple-mark wherever water is oscillating over sand, whether its surface be smooth or uneven to start with. These last two, therefore, are clearly the *essential* methods, while accidental unevennesses of surface merely delay uniformity in the results.

4. *The Origin of the Ripple Vortex.*—Since the ripple vortex with its neutral line and brush plays such a large part in the initiation as well as in the growth of ripple-mark, it is clear that the causes of its formation and the laws of its development must be traced before any satisfactory theory of ripple-mark can be evolved. It is, as is shown in fig. 4, a spiral vortex composed of a ribbon of water wound round a cylindrical core, just as the mainspring of a watch is wound round its barrel. And one very curious fact that I observed about it was that it did not come into play in the beginning, but only during the latter part of each swing.

I had some difficulty at first in imagining how such vortices could arise, and sought in vain among all the vast number of papers on vortex motion

that have been published within the last thirty years for some light on the subject. These appeared mostly to bear on vortices already formed, and moving in a frictionless fluid of infinite extent. Few dealt with any real fluid, and none, that I could find, with the process of formation of the vortex. Prof. Darwin traced analogies between the ripple-forming vortices and those set up by an oar in sculling, and by the motion of a fish's tail; but nowhere could I find any suggestion as to the actual process by which the vortices were generated.

Finally, I formed the hypothesis offered below, which is, I consider, confirmed by the experiments on the early stages of ripple-vortex formation presently to be described. When the impulse is in the direction AB, say (fig. 5), the water in the lee of a ridge, DE, is more or less protected from the impulse by the ridge, and therefore the water below D moves much more slowly than that above.

The first jerk of the impulse moves the water away from DE to EF, say, and then friction between the quick and the slow water enables the former to continue to drag the latter away from the ridge, and thus to keep up the diminution of pressure between DE and EF. The balance of pressure is, of course, immediately restored by a flowing in of water from other parts. *This diminution of pressure in the lee of a ridge is one of the two necessary conditions for creating a ripple vortex there.*

To find the other condition we must consider where the water comes from that flows in between the ridge and the water in its lee, when the pressure there is diminished.

In every mass of water oscillating about a single place of constant level, each swing distinctly divides itself into two parts—the first part (*a*, fig. 5), in which the higher half of the water falls, and the lower half rises to the average level; and the second part (*b*, fig. 5), in which that which was the higher half falls *below*, while that which was the lower half rises *above* the mean level. Thus, during every instant except the single one in which all the water is at the same level, the pressure exerted by every element of the water is compounded of two—one due to the velocity it has already acquired, and the other to the difference of level of the water at the moment. The second, which may be called “gravity pressure,” is always, of course, exerted from the side on which the water is highest towards that at which it is lowest; and when there is a sudden attempt at a diminution of pressure at any one particular point, the direction of the gravity pressure at that point along each special line must be from the plane of highest level to the point. The gravity pressure at D, along the line PQ, for instance, when the pressure is diminished at D, must act from P towards D, and not from Q

towards D, and similarly all the arrows in *a* and *b* (fig. 5) indicate the directions of the gravity pressures at D, along their own particular lines. In

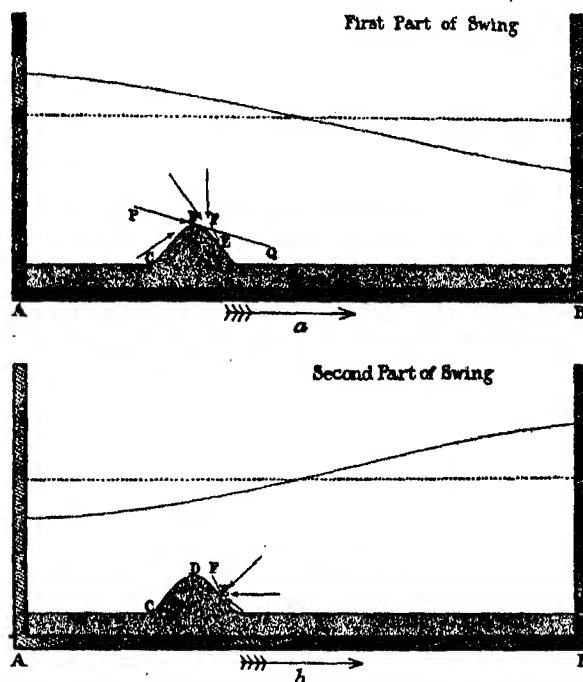


FIG. 5.—Diminution of Pressure between Ridge and Water and Direction of Gravity Pressure during Swing from Left to Right.

other words, when the pressure is suddenly diminished at any point in the water, the direction of the resultant gravity pressure at that point is from the end where the water is highest towards the point.

The effect of the gravity pressure on the flow of the water, when the pressure in the lee of a ridge is diminished by the drag exerted by the flowing water on the still water, can now be readily traced with the aid of fig. 5. The ridge is behind, and the water is being pulled away from it in front, so that water to fill the space can only flow from above or below. In the first part of the swing (*a*, fig. 5) the water below D can clearly exert no pressure along DE, and therefore it is only that above D which counts. This has a resultant gravity pressure along DE in a downward direction, which must impart at each instant an additional downward velocity to that which the water already possessed. Thus all the forces acting on the water in the first part of a swing tend to move it roughly in the same direction, and so no vortex then forms—the moving water simply sweeps over the ridge, pressing as closely as it can get against its lee side DE.

In the second part of the swing, when the water is highest on the *lee* side of the ridge, matters are very different—now the gravity pressure *opposes* the flow of the water, and its resultant along DE evidently points up the ridge (*b*, fig. 5), so that with a diminution of pressure at D the water close to the ridge flows in the opposite direction to that at a little distance from it, and so a vortex is created. *Thus the second condition for the formation of a ripple vortex is that the resultant gravity pressure along the ridge on its lee side shall tend upwards.*

As a test of the correctness of the explanation suggested above I studied some ripple vortices in water that was very shallow, and that therefore moved extremely slowly. As, under these conditions, pepper did not indicate the stream lines of the water with sufficient delicacy, I had recourse to crystals of permanganate of potash, each of which sent forth a steady stream of colour for several minutes, which indicated the flow lines of the water with great fidelity.

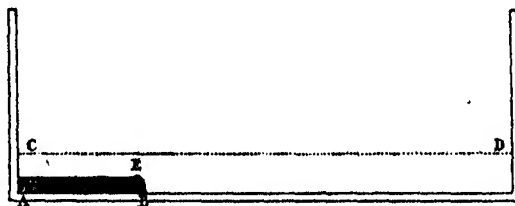


FIG. 6.—Arrangement for Watching Formation of Ripple Vortex.

To ensure a slow motion of the water I had it less than an inch deep, and, in order that my eye should not be distracted by vortices in both directions, I arranged the trough as seen in elevation in fig. 6. AB was a barrier which extended transversely across the trough but ended abruptly in a steep descent nearly parallel to the end of the trough. CD was the level of the water when at rest. At E a crystal of permanganate of potash was placed, protruding very slightly from the barrier. With this arrangement a good vortex formed when the swing was from left to right, but none, naturally, when it was from right to left.

The following was the process of formation in the left to right swing. When the swing began, a thin straight stream of coloured water flowed over the ridge, obviously filling in the gap made by the moving away of the water that was nearest the side of the ridge (*a*, fig. 7, Plate 3).^{*} Next, when the water began to rise on the right-hand side, the flow over the top of the ridge became nearly horizontal (*b*, fig. 7), and, as the water beyond the

^{*} The end of the barrier and the water near it only are shown in the photograph.

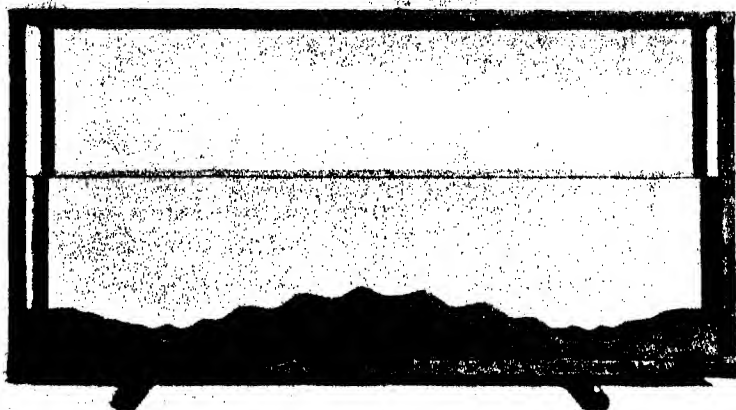


FIG. 1.—Vertical Section of Mound raised from Level Sand by Oscillating Water.

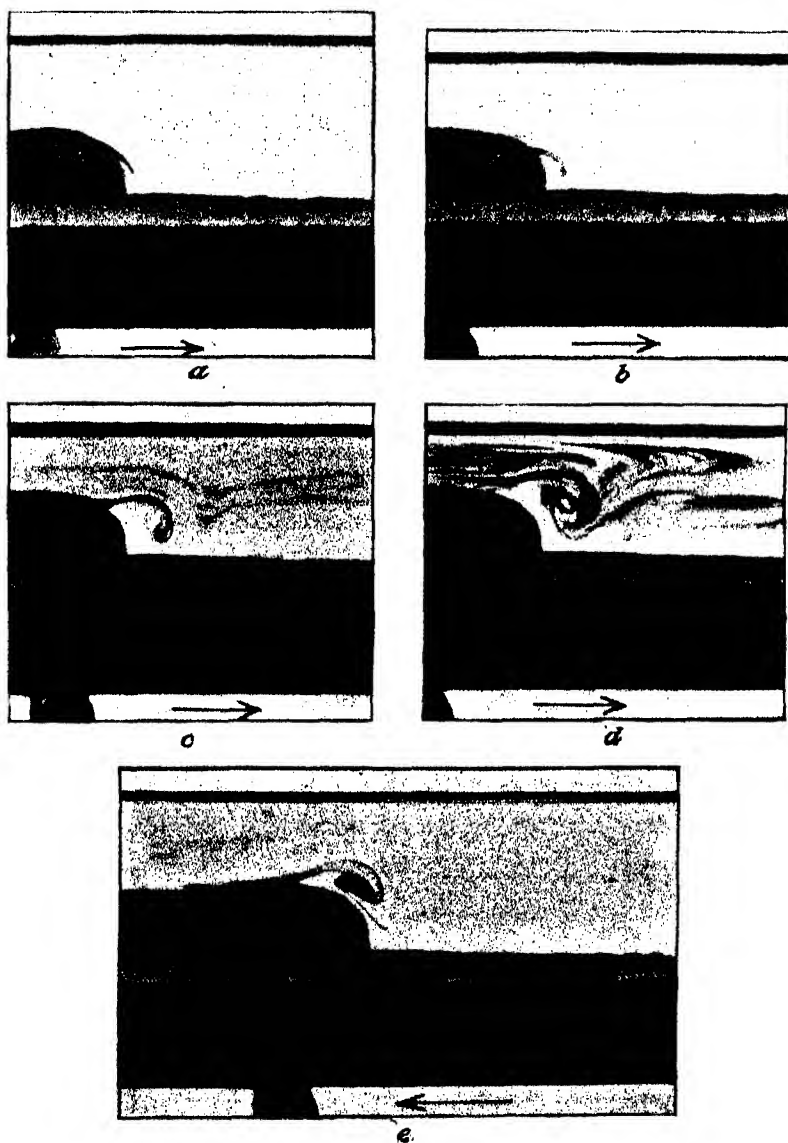


FIG. 7.—Different Stages of Formation of the Ripple Vortex.

ridge rose above the mean level, the downward-moving coloured stream retreated upwards as if being pushed up—as it undoubtedly was by the pressure of the higher water in front of it—the end of the horizontal branch curled back towards the ridge, forming a spiral, and the vortex was complete (*b, c, d*, fig. 7). Thus my hypothesis was confirmed in every particular. (In *e* (fig. 7), the direction of flow having changed, the vortex is being raised and tossed back along the barrier.)

There remained one further experiment to try in order to obviate all possible doubt. If, as I had surmised, and as the above experiments seemed to prove, it was necessary for the gravity pressure to *oppose* the flow of the water for the vortices to form, then no vortices of the kind I have described could be created by water flowing *steadily* in one direction over an obstacle, for in that case gravity pressure would always *aid* the flow of the water.

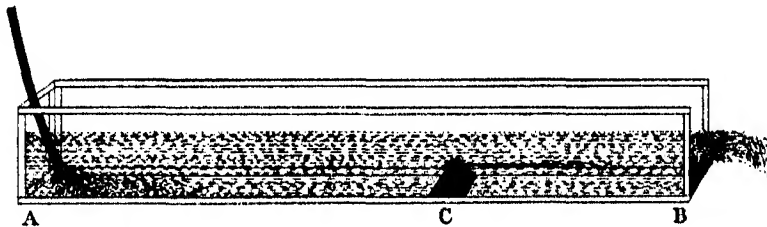


FIG. 8.—Coloured Stream from Crystal of Permanganate of Potash on Summit of Ridge over which Water is flowing steadily in one direction.

In making this experiment I used a trough, A B (fig. 8), open at one end, B, so that, if necessary, the water could flow out as fast as it flowed in. Water was led through an indiarubber tube into the closed end, and flowed out at the open end. A ridge of sand, C, extended across the trough nearer the open than the closed end, a good distance being left between it and the tube, so that the flow should become as steady as possible before the water passed over the ridge.

Closing the open end up to about twice as high as the ridge, so that still water rested against the ridge, the stream of colour from the crystal placed on the summit of the ridge flowed exactly horizontally for distances varying between 1 and 2 inches, according to the steadiness of the water, and then finished in a curious flickering motion, which is shown as nearly as possible in fig. 8*. Lowering the end barrier made no material difference in the appearance of the coloured stream, but when it was completely removed the

* It is impossible to give an exact representation of this motion, because tiny water ripples came and went and flickered almost like the flame in a coal fire, which is now in one place, now in another.

rush of water flattened the sand ridge very considerably, still leaving the lee side very steep, however, and then the surface of the water was permanently lowered, and it rippled just beyond the ridge, but no ripple vortices were formed.

Finding that no water streamed down the ridge when the flow was steady, I concluded that the friction between the flowing and the comparatively still water was not sufficient to move the latter under steady conditions, but that a jerk was required to overcome the inertia of the stiller water. To try if this were so I gave the flowing water an impulse by pushing it along towards the ridge with a slip of wood the width of the trough. The result was that a small stream of colour immediately appeared against the side of the ridge, and, as soon as the water in front of the ridge rose higher than that behind, a vortex formed.

These experiments appear to me to prove conclusively that the creation of ripple-forming vortices depends entirely upon the two conditions I have formulated, viz.: (1) the establishment of a diminution of pressure in the lee of an obstacle; and (2) the turning down and back again of the water that has flowed over the ridge, through the backward pressure on it of the water that is temporarily raised above the main level in the far end of the vessel.* Thus ripple vortices depend for their existence on variations in the gravity pressure of oscillating water that obviously must exist, but the importance of which in connection with the formation of vortices has not, perhaps, before been recognised.

It has hitherto been supposed that a uniform steady current of sufficient velocity was capable, unassisted, of generating vortices, both of the sand-raising type and of other types, when flowing over an uneven sandy bottom. My experiments given above, and others that I hope to publish later, show, however, that although the water in the lee of an obstacle over which there is a steady flow is disturbed, *no definite vortex in the least resembling a ripple vortex forms there. Hence a steady current is unable either to generate or to maintain ripple-mark.*

5. *Different Intensities of the Ripple Vortices.*—The ripple vortices have not all the same intensities, and at the ends of the vessel they even differ so widely on the two sides of the same ridge that the vortex facing the middle of the trough in one swing is incapable of moving the sand, while the end-facing one in the next swing raises a pretty little sand vortex. A little consideration shows that this must be so.

Ripple vortices are caused by a current flowing over the summit of a ridge

* I am aware that this explanation has been contested, and I offer it entirely on my own responsibility.

away from its lee, acted on by a pressure exerted *towards* the lee. The rotational velocity of the vortex must depend upon the horizontal speed of the current and the magnitude of the pressure combined.

Now the horizontal velocity of the current increases from zero at the near end of the vessel (the end at which the impulse is given) to a maximum at the middle, and diminishes to zero again at the far end. Hence, if the nine

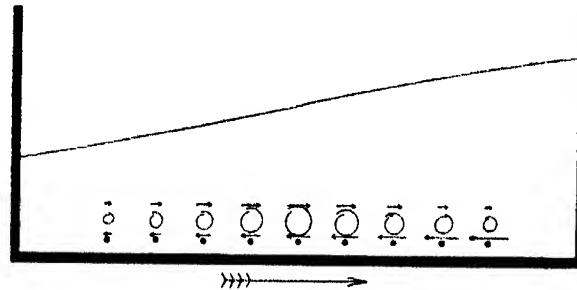


FIG. 2.—Rotational Velocities of Vortices at the same Instant in Different Parts of Trough during Swing from Left to Right.

dots in fig. 9 represent the summits of ridges during the second part of a swing from left to right (remembering that no vortices form in the first part of the swing), the upper arrows will represent the direction, and their lengths, roughly, the relative horizontal velocities of the current. Again, since the greatest gravity pressure is always at the far end of the vessel, in the second part of the swing, this pressure is least at the near end of the trough, and increases continuously to the far end, so that the lower arrows in fig. 9 give the direction of the motion imparted by the gravity pressures, and their lengths represent roughly the relative values of those pressures. Thus, both current and pressure are small at the near end of the vessel, but, while both increase up to the middle point, beyond that the current diminishes and the pressure continues to increase. Hence, in a swing from left to right, the rotational velocities of the vortices must be roughly proportional to the sizes of the vortices in fig. 9—that is they increase from the near end up to the middle ridge, and then diminish again to the far end, but each is larger on the far side than the corresponding one on the near side of the vessel. In the next swing—from right to left—the relative velocities of the vortices on the two sides of the vessel would, of course, be changed, so that the smallest vortex was now on the right-hand side of the ridge. It is clear, therefore, that while the rotational velocity of the end-facing vortex of a ridge is always greater than that of its middle-facing vortex, both are swifter the nearer the ridge is to the middle of the vessel.

6. *Initial Ripple-distance*.—Prof. Darwin observed that the ripple-distance increased with the number of oscillations of the water after its initiation, but, in the absence of any information as to the process of initiation, it has been impossible for any one hitherto to judge of what determines the first distance of one ripple from another. We can now, however, ascertain this from a consideration of the laws governing the lee vortex and its brush.

In smooth and level sand with a single ridge in it, the first swing of the water causes a vortex to form in the lee of this ridge, the brush of which sweeps together a line of sand that is the nucleus of a new ridge (fig. 4, p. 290). Clearly the distance between this new ridge and the old one is determined by the final size of the vortex in that first swing and the distance between its neutral line, D (fig. 4), and the new ridge, EF, which distance I shall call the sweep of the brush. As this latter is the more important factor of the two in determining the ripple-distance I shall deal with it first.

The Sweep of the Brush.—The sweep of the brush depends upon two things, viz., the velocity of the water that forms it and the room it has to spread in. From the nature of the brush its velocity must vary with the horizontal velocity of the water passing over the ridge, and this is greatest in the middle of the vessel, greater the greater the amplitude of the wave, and, since the horizontal velocity varies less, in different parts of the vessel, the deeper the water, the sweep of the brush also varies less, in different parts, the deeper the water.

The room the brush has to spread in evidently depends, not only upon the length of the trough and on where the generating ridge is in the trough, but also upon whether the vortex is on the end-facing or the middle-facing side of the ridge. Thus the sweep of the brush is greater—

- (1) the longer the trough, *i.e.* the greater the length of the stationary wave,
- (2) the farther the lee side of the generating ridge is from the end that it faces of the vessel,
- (3) the greater the amplitude of the wave.
- (4) It differs less, in different parts of the vessel, the deeper the water.

The Size of the Vortex.—As the vortex is a band of water wound round a cylinder of originally stiller water, its size at any given instant is greater the larger the cylinder is to start with, the more quickly it is wound and the longer it spins.

Now the thickness of the cylinder to start with depends on the height of the generating ridge, within certain limits to be determined later. The

velocity with which it is turned has been shown to depend on the horizontal velocity of the water that rubs the sand, and on the backward gravity pressure, both of which are functions of the amplitude of the wave and of the position of the vortex in the trough and on the ridge. The duration of the vortex depends upon the periodic time of oscillation, which bears a direct relation to the length of the trough and is an inverse function of the depth of the water.

The vortex is larger, at any instant, therefore—

- (1) the higher the generating ridge (within limits),
- (2) the greater the amplitude of the wave,
- (3) the nearer the generating ridge is to the middle of the trough.
- (4) It is greater on the end-facing than on the middle-facing side of the generating ridge.
- (5) It is greater the longer the trough and
- (6) the shallower the water (within limits).

The conditions necessary for the vortex to be large, then, are very similar to those required for the brush to have a long sweep, except in one particular—the vortex is larger on the end-facing side of the ridge, and the sweep longer on its middle-facing side. When two conditions are at war, experiment must prove which gets the upper hand. I used my artificial ridge to try this, and found that the new ridge created on its middle-facing side was always farther from it than the one created on its end-facing side, but that the two distances differed less the nearer the artificial ridge was to the middle of the vessel.

We can now, by combining the conditions necessary for the vortex to be large with those requisite for the brush to have a long sweep, find out how the initial ripple-distance varies with varying conditions. This distance must increase with—

- (1) the height of the generating ridge (within limits),
- (2) the amplitude of the wave,
- (3) the nearness of the generating ridge to the middle of the trough,
- (4) the length of the trough, or of the stationary wave,
- (5) the shallowness of the water (within limits).
- (6) It is greater on the middle than on the end-facing side of the generating ridge.
- (7) It differs less in different parts of the vessel the deeper the water.

The two limits mentioned above are the following :—

- (1) If the first ridge is so 'high that the velocity of the water is only sufficient to move a small portion of the slack water in its lee, the diameter

of the cylindrical core is determined by the velocity of the water instead of by the height of the ridge. In that case the new ridge rises *on* the first one instead of beyond it.

(2) When the water is so shallow that its friction is insufficient to move the particles of sand, no ripples form.

7. *The Growth of Ripple-mark.*—Let BCD (1, fig. 10) be a ripple and AB, DE, the sides nearest to it of the two neighbouring ripples, when the water was at rest; what is seen when it is oscillating is this:—

In a swing, from left to right, say, at the first instant no vortex forms on either side of BCD, sand is simply pushed up BC, and a little is washed off the summit C, and thrown or dropped anywhere between C and E (2, fig. 10). Next a vortex forms against CD, which is made apparent, if the motion is strong enough, even without the use of pepper, by the whirling round of the sand scooped out by it from the lower parts of CD (3, fig. 10), and by the movement of the sand up DC against the general flow of the water. At the same time sand continues to be pushed up BC to the summit, where a part of it rests, while the remainder slides over to the other side, and, being kept from falling by the vortex, gathers into a small ridge such as F (3, fig. 10). Then when the swing changes, the sand in the vortex rises, spreading out as it goes (4, fig. 10). The part of this sand that touches the summit C remains there, and the rest is carried along to the left, to a distance varying between a fraction of an inch and several inches, according to the horizontal velocity of the water and the periodic time of the oscillation. Wherever this vortex has reached when the swing changes, all the sand that has not fallen by the way is deposited, unless the motion is so violent that some is carried back again in the next swing, before it drops. The first flow of the water in the new swing also sweeps the ridge F up to the summit and leaves it there (4, fig. 10), so that this helps to raise the summit. After this a vortex forms against BC (5, fig. 10) as it did previously against CD, and at the end of the swing the ripple resembles BCD (5, fig. 10), B being lower and C higher than in 3 (fig. 10). Thus every swing raises the summit and lowers the base of the ripple and so increases its height doubly. When the oscillations are allowed to die away, the small ridges at F and G raised by successive swings are smaller and higher up with each oscillation, till, when the water comes to rest, the ripple resembles 6 (fig. 10), C being higher and B lower than when the oscillations started.

All this is what is *seen* when ripples are growing under oscillating water. The explanation of most of it is obvious, from what has gone before. The first instant of observation, during which no vortex forms, is what I have called the first part of the swing—the time when the water is gaining its

mean level, and there is, consequently, no backward gravity pressure. The next moment, when the sand vortex forms, is what I have called the second

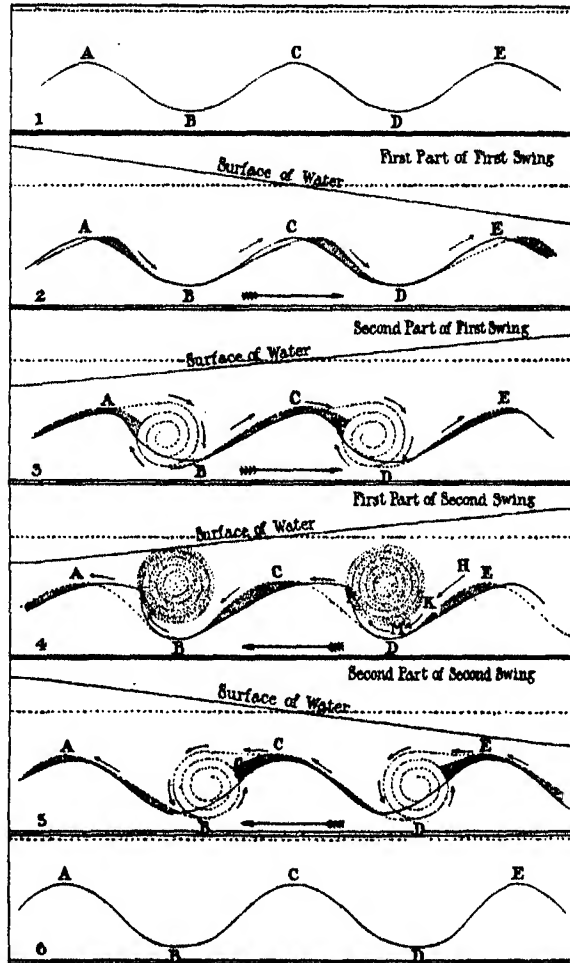


FIG. 10.—Various Changes in Size and Shape of Ripple produced by one Complete Oscillation of the Water.

part of the swing, when the water is rising above its mean level, and there is, therefore, a backward gravity pressure. The only part of the operation that has not already been accounted for is the expansion and rise of the vortex when the swing changes. This I explain in the following way:—

The vortex is formed and grows under pressure from the onward flowing water above and the backward pressed water below. At the moment when the swing changes, the water as a whole comes to rest, with the result that the downward pressure of the flowing water is taken off the vortex, while the

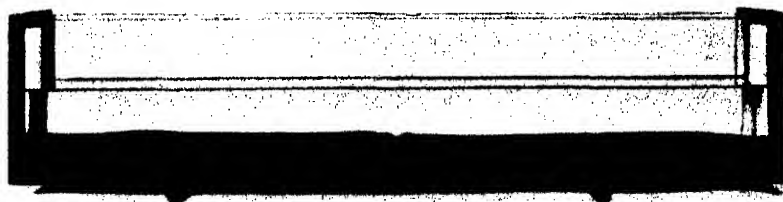
upward pressure from the raised water remains (HKM, 4, fig. 10). The moment the downward pressure is taken off, the vortex expands, I imagine owing to its centrifugal force, and is raised upward by the pressure of the high water, and it is then swept onward in the new direction with the new swing.

8. *The Motion of each Ripple as a Whole.*—Concerning the growth of the ripple-distance, Prof. Darwin says: "On the parts of the plate where the sand is thick, a continual rearrangement of ripple-mark goes on; the wave-length extends by the excision of short patches of intercalated ripple-mark, and by general rearrangement. Finally, the sand reaches an ultimate condition as regards wave-length, although rearrangement of ripple-mark still appears to go on for a long time."

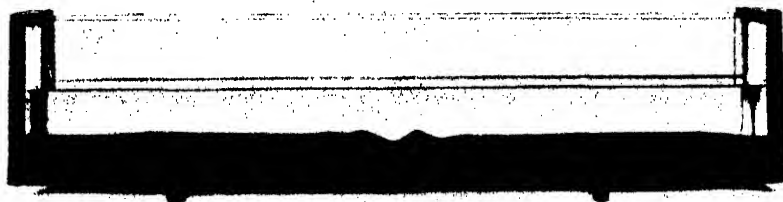
My own earlier observations apparently accorded with this description, but, wishing to find out more definitely exactly how the rearrangement took place, I started *de novo* with smooth level sand, in the middle of which I had artificially made two ripples as starting points for other ripples. These were raised by pressing a thin slip of wood down into the sand and then withdrawing it, after moving it slightly to each side, to pile up the sand (*a*, fig. 11, Plate 4). The ripples were about half an inch high on the inner side to begin with. With this arrangement I was led to the following new results:—

After a few oscillations, each of the ridges (*b*, fig. 11) was half an inch or so farther from the middle of the vessel than at starting, while the two new ridges that one would have expected, from what has gone before, had formed to the left and right of them.

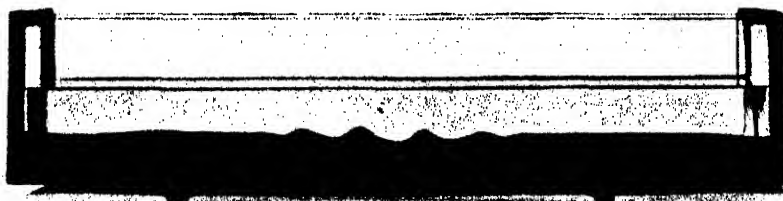
Further oscillations increased the spaces between all the ripples, as well as producing more ripples to the right and left of them (*c*, fig. 11). Thus, for a short time after its initiation, each ripple travels farther from the one that generated it, and, consequently, from the middle of the vessel, with every oscillation. After a little while—some time before the whole of the sand was rippled—the summits of the two ridges that were nearest the middle of the vessel first became stationary, and then began to move back *towards* the middle with each oscillation. Next the same thing happened to the next ridge on either side of the middle ones, and finally—soon after the whole of the sand had become ripple-marked—all the ripples were travelling *towards* the middle of the trough. Now it is obvious that if all the ripples travel *towards* the middle of the vessel, at least two of them must at last coalesce, and then two others, and so on; and this does actually happen. As soon as two ridges get so close together that the vortex of one can snatch sand from the summit of the other, while that other, from inferiority either of size



a



b



c

FIG. 11.—Motion of Ripples immediately after Initiation.



FIG. 13.—Longitudinal Scoring of Sand Ripples.

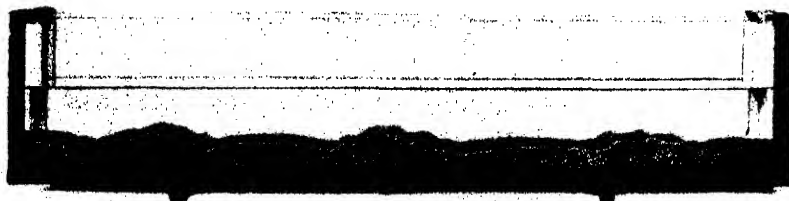


FIG. 14.—Sand Mounds formed by Water Oscillating in Stationary Waves two-thirds of the Length of the Trough.

or position, or both, is incapable of returning the compliment, this second one quickly gets swallowed up, and its sand goes to swell its rival. These coalitions generally take place at or near the middle of the trough, and they would naturally always do so but that the sand, water, and impulses are never perfectly symmetrical. For the same reason the whole length of a ripple seldom gets absorbed at the same time. It is usually higher in one part than

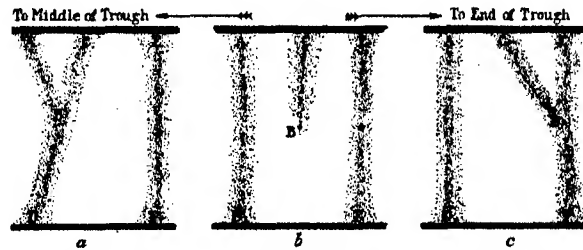


FIG. 12.—Formation and De-formation of Y-shaped Ripples. Plan.

in another, and then the lower part disappears first, while sometimes the higher joins on to the demolishing ripple that is on its end-facing side, as shown in plan in *a*, fig. 12, where *AB* is the part, and *CD* the whole ripple that it joins. When this happens, succeeding oscillations usually bring *AB* and *BD* into line, cutting off *CB* (*b*, fig. 12), which then joins the next ripple (*c*, fig. 12), when the same process is repeated, and *EB* is cut off and joins the next ripple, and so on till at last the cut off part either becomes absorbed or obliterated, or it grows into a full-sized ripple at the end of the trough.

For some little time after the whole sand has become rippled, in a trough, the ripple-distance at the ends is only slightly less than at the middle; but as the height of the middle part of the sand grows, while that of the ends diminishes, under continued oscillation, the ripple-distance increases in the middle while it diminishes at the ends, so that at last the series of ripple-distances is graduated from very small—perhaps half an inch or so at the ends of the vessel to three or even four inches in the middle. All these changes of ripple distance are entirely effected by the coalition of ripples just described, together with the formation of new ripples at the ends of the trough, and these two phenomena are due to the *motion* of the ripples as wholes, which is brought about in the following manner:—

It is easy to see that the motion must be connected with the transference of sand from one side of a ridge to the other and back again during each oscillation (fig. 10, p. 301). If more sand were always deposited on the right side in one swing than was swept back on to the left side in the next, for instance,

the middle plane of the ridge would travel from left to right, and the whole ridge would therefore do likewise; and, *vice versa*, an excess of sand placed on the left side would lead to the motion of the ridge from right to left. I shall now show that this unequal transference of sand is exactly what *must* take place among a series of ripples.

It has been seen that during the second part of a swing (3, fig. 10) a vortex scoops up sand FD from the lower part of one side of a ridge, and that during the first part of the next swing it carries this sand over to the other side of the ridge, together with a slice of sand which it cuts off from the upper part of the first side (4 and 5, fig. 10). The amount of sand scooped out by the vortex is greater the larger and swifter the vortex; also the slice of ridge carried over the summit with the vortex sand increases with the depth of the side of the ridge and with the longitudinal velocity of the water, and is greater when this velocity is increasing than when it is diminishing.

Now, I have shown that in established ripple-mark, the end-facing vortex of a ridge is always larger and swifter than its middle-facing vortex. Also, the flowing water has always an increasing longitudinal velocity when it is washing sand from the end-side to the middle-side of a ridge, since it is then travelling *towards* the middle of the vessel, and a diminishing velocity when it is carrying the sand in the opposite direction, *away* from the middle. It follows, therefore, that in established ripple-mark, more sand must be transferred from the end-side to the middle-side of a ridge in one oscillation than is conveyed back again to the end-side in the next oscillation, and it is for this reason that the ridge, as a whole, travels towards the middle of the vessel. In fact, *each established ripple partakes, as a whole, of the general movement of the sand towards the places where the longitudinal velocity of the water is a maximum.* It is thus apparent that, unless there is little enough sand for it all to collect at the middle, the ripples must continually re-arrange themselves, not only for a time, but for as long as the oscillation is continued, or till the sand is piled up in such a way that ripples are no longer possible.

The apparently anomalous cases when the ripple moved away from the middle are readily explained. These were: (1) when the first two ripples were made by pressing a slip of wood down into the sand in the middle of the vessel, so that the furrow between the ridges was deeper than the furrows on their other sides (*a*, fig. 11); and (2) when a new ripple was generated by the end-facing vortex of an existing one (*c*, fig. 11, Plate 4). Both these ripples had deeper middle-side than end-side furrows—the first, because it was specially made in that way, and the second, because the vortex on the

middle-facing side of the ridge had scooped out the furrow below the mean level of the sand, whereas no vortex had yet existed on the end-facing side, which was merely a small pile swept up above the level of the sand (*b*, fig. 11). Hence, at first, the end-facing vortex of each ripple was smaller than its middle-facing vortex and the end-side of the ridge was shallower than its middle-side, for both of which reasons less sand was at first scraped off the end-side of the ridge in one swing than was returned to it, from the middle-side, in the next; and, consequently, the ridges travelled endwards. As, however, the end-facing vortex has always a greater rotational velocity than the middle-facing vortex (see p. 297), the end-side furrow deepened more quickly than the middle-side one. Hence, the disparity in the quantity of sand that was scraped off each side alternately gradually disappeared, and when this became equal the ridge became stationary. As the end-side furrow still continued to deepen more rapidly than the middle-side one, however, *more* sand was now scraped off the end-side than was returned to it, and so the normal state of things was brought about, viz., the ridge travelled as a whole towards the middle of the vessel.

In order to test the validity of the foregoing argument, I made two ripples in the middle of the vessel by scraping up sand from both ends, and then pressing down the slip of wood into the middle of the resulting dune, so that the end-sides of the two ripples thus formed were longer than their middle-sides. The result was as I expected. After a few oscillations, instead of the two dunes having separated further, they had coalesced and become one, through each having moved towards the middle.

Other experiments of the same kind, such as making a ripple about half-way between the end and the middle, and first having its deeper furrow on the end-side, and then on the middle-side, were equally successful; for, in the first case, the ripple moved towards the middle, and in the second, towards the end of the vessel.

9. *Side of Ripple facing Shore Steeper than Side facing Sea.*—The unequal sizes of the vortices on the two sides of a ridge and the unequal transference of sand from one side to the other naturally affect the shape of the ripple. The larger end-side vortex hollows out a deeper end-side furrow, tending to make the end-side of the ridge steeper and deeper than the middle-side, a tendency that is strengthened by the greater transference of sand to the middle-side, and that is still further accentuated by the sand dropped by the travelling vortices, which naturally rests more easily on the gentle slopes than on the steep ones (fig. 1, Plate 3). This is the reason that the ripples on the sea shore generally have steeper slopes facing the shore and gentler slopes facing the sea. The shore takes the place of the end of the vessel in checking

the flow of the water, so that the shore-sides are the end-sides of the ripples, and the sea-sides are what I have called their middle-sides.

10. *The Longitudinal Markings of Rippled Sand*.—Sand ripples are never entirely smooth, they are marked with small irregular longitudinal ridges and grooves, almost as if they had been combed (fig. 13), more especially when the motion of the water is fairly violent. This is due, I think, to the vortices not having the same cross-section throughout their whole length, but being rather like beads of varying diameters strung on the same horizontal wire, so that they scoop out the ridges to unequal depths, according to the cross-section of the beads. With unequal cross-section of the vortices, the brushes would be unequal also, and so they would dig to different depths into the weather sides of the ripples. Thus, both sides of the ripples would be scored. The following is the way in which I believe the vortices obtain their varying cross-sections:—

During their growth they have to sustain the weight of such ridges as those marked F (fig. 10, p. 301). But from accidents of slipping this ridge has very varying weights in different parts. Where the weight is heavy, the sand slips further, and the vortex is necessarily smaller than where it is light. Hence, each vortex is not single, but is composed of a series of vortices of different diameters set end to end.

When the swing changes, the series breaks up into a number of separate small vortices, each having its axis inclined to the horizontal at some angle that depends upon the contour of the sand against which it was twirling at the moment when the swing changed, and it was pushed back and up. The inclination of the axis to the horizontal is sometimes so great that it actually becomes vertical, and but few of the vortices remain horizontal after they have begun to travel.

11. *Travelling Vortices*.—We have now traced three steps in the advance of the sand from the ends to the middle of the vessel:—

(1) Before the ripples have formed, every complete oscillation of the water leaves each single grain that is moved nearer to the middle than it found it.

(2) While the ripples are forming, the same process goes on in the parts of the sand where ripples have not yet appeared; but, where they have, each ripple is removed *farther* from the middle with every oscillation.

(3) When the whole sand is ripple-marked, every oscillation leaves each whole ripple nearer to the middle than it found it.

There remains one more step to complete the series. When the vortices are carried away from their generating ridges, after each new swing, it is the large vortices from the *end-facing* sides of the ridges that are transported towards the middle of the trough, while the small ones from the *middle-facing* sides

are taken in the opposite direction. The sand that is continually dropping from them, therefore, falls more thickly on the middle of the vessel than on its ends, so that in this way also the gathering of the sand in the middle is accelerated. Thus, every operation performed by the water—except one which is purely temporary—tends to drive the sand from the ends to the middle of a vessel, when it is oscillated in such a way that the water level remains constant in the middle, and has its maximum variations at the ends. No wonder, then, that the sand soon becomes banked up in the way shown in fig. 1.

12. *Ripple-Mark on the Sea-Shore.*—For the ripple-mark that I have hitherto considered, one of two conditions was necessary to start the ripples. Either the oscillating water had to have at least one constant place of maximum longitudinal velocity, or there must be at least one obstacle or hollow in the sand to give birth to vortices. Of obstacles in the shape of stones, bunches of seaweed, etc., as well as of hollows, there is generally no lack on a sandy shore, but the question arises—would a beach that was entirely smooth and featureless to begin with become ripple-marked when the sea oscillated over it? Obviously it would, for in order to start a primary ripple it would only be necessary for the water to have a maximum longitudinal velocity at or near the same place during a few successive oscillations, so that even a single one of the smallest of small primary ripples could form. Once this was done, other ripples, as I have shown, would arise as a matter of course, until the whole sand was covered with ripple-mark; and the ripple-mark would be very regular, for although the places of maximum horizontal motion of the water would often remain the same, or nearly the same, for a short time, yet they would not usually remain so long enough for such mounds as those shown in fig. 1 to form. On the contrary, the velocity and back gravity pressure of the water flowing over any individual ripple must be continually changing, so that on the average each is subjected to the same influences, and their heights and ripple-distances are therefore fairly equal after any single tide. But as the heights and ripple-distances of all vary with the amplitude of the wave, they are greater after a storm than during calm weather.

In order to try and imitate the action of the sea on an originally smooth sandy beach, I used about an inch of sand made quite smooth and level in my 36-inch trough, with about 2 inches of water above it. I then alternately raised and lowered one end of the trough, bit by bit, giving it a slight jerk at each rise or fall, to make the water oscillate, but allowing several oscillations to take place between each jerk. In this way not only did the place of maximum longitudinal motion differ slightly for each

oscillation, but the depth of the water changed at the same time, which is exactly what happens in the sea. When this was done for some time, the sand remained level on the whole, but became covered with very regular even ripple-mark, just like that of the sea-shore; and, as was to be expected, the sand did not rise higher, on the whole, in any one place than in any other.

It might be objected that, since all the conditions for the formation of ripple-mark appear to exist in every place where there is a sandy beach washed daily by the tides, ripples ought to be much more universal in such places than they are. The reply is that they *are* universally *made*, but that most of them get smoothed out by the edges of the waves of the retreating tide, and only remain intact in pools or depressions of any kind, where the water, being temporarily left by the retreating tide, sinks slowly and uniformly downwards through the sand.

13. *Ripple-Mark under Stationary Waves*.—In my earlier experiments the trough was oscillated in the simplest possible way, *i.e.* so that the length of the stationary wave was twice the length of the trough. Subsequently it occurred to me that by oscillating more quickly I ought to be able to get smaller stationary waves, the effect of which on the sand would be to produce groups of ripples at or near the loops of the waves, where the longitudinal velocity was a maximum, and to leave smooth spaces at or near the nodes, where it was a minimum. In this I was successful, and fig. 14, Plate 4, shows the effect when the stationary wave was two-thirds of the length of the trough instead of being twice as long. Ripple-marked mounds rose at the three loops, where the level remained constant and the longitudinal velocity was a maximum, and smooth spaces remained at the four nodes. By oscillating the trough with different velocities I was able to obtain from one to seven mounds, with clear spaces between, at will.

The height to which a mound can rise when the water has a given minimum depth and the quantity of sand is practically unlimited depends solely on the length of the stationary wave. This wave-length settles the distance between the mounds, and this distance determines the height to which a mound will rise before some of it slips down, or before the weight of the highest part makes it spread out laterally, thus partially filling up the space between it and the next mound, and so diminishing its height again.

The following is what happens when oscillation is prolonged:—If the sand is thin, it collects in separate mounds at the places of maximum longitudinal velocity, leaving the bottom of the vessel bare between. If the sand is of practically unlimited thickness it rises to a certain height

at each of such places, and then broadens on the top into a sort of tableland, smooth at first, but covered with irregular ripple-mark afterwards. When this happens, the mound has reached the maximum height it can attain to under the given conditions. Soon sand slips somewhere, and the whole shape changes somewhat, and then rebuilding goes on, till the same height is reached again, and then another slip occurs—sometimes two or three in different places—and rebuilding starts afresh. There is thus no *exact* height which the mound *retains*, but it has a *maximum* height for each wave-length, provided the water has a certain minimum depth above the top of the mound when it is at its highest. Increased amplitude of the wave hastens the attainment of this height, while greater depth retards it; but nothing but a change of wave-length *alters* it, I think.

When the oscillation is very regular, the bare spaces between the mounds remain entirely free from ripple-mark, as in fig. 14, Plate 4, but if it is at all irregular, there are no parts of the sand where the level of the water remains *quite* constant, and then a series of ripple-marked heaps rise which are separated by no smooth spaces.

In shallow water, after a time, the tops of the mounds become flat, and the furrows then look like grooves cut for irrigation purposes. In one case, for instance, the mounds finally became quite flat-topped, with runlets between, as shown in profile in fig. 15.

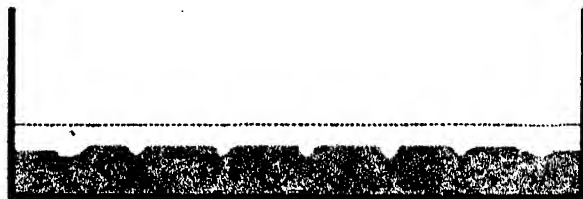


FIG. 15.—Flat-topped Mounds with Grooves between, produced by Prolonged Oscillation with Stationary Waves in Shallow Water.

The process described above, by which mounds of sand are built up under the action of stationary waves, may be summarised as follows:—

- (1) Ripples always first form at places of maximum longitudinal motion of the water, *i.e.* at places of constant level.
- (2) Smooth spaces are left at and near the places where the water has no longitudinal motion, that is, where the change of level is greatest.
- (3) Each set of ripples grows into a mound, having its centre plane at the place of maximum longitudinal velocity and its lowest parts close to places where the longitudinal motion is zero.
- (4) There are therefore two of these mounds to each water wave.

After having arrived at the above conclusions, and proved them experimentally, I found that C. de Candolle,* in a long and most interesting paper on the subject, had mentioned that, under stationary waves, he had observed groups of ripples with smooth spaces between. He said: "Lorsqu'il existe dans l'auge plusieurs ondes stationnaires, il se forme autant de systèmes de rides qu'il y a de ces ondes" (this would only be correct if C. de Candolle used the term "onde" to signify a half of what we call a stationary wave). He continued: "Et ces rides sont groupées de part et d'autre de *chaque plan vertical séparant deux ondes contiguës.*" [The italics are mine.] This appears to be vague, but the context shows that C. de Candolle meant the places of constant level, and it is, therefore, a true description. He appears, however, to have failed to notice the most important point about these groups of ripples, namely, that they finally grew into mounds, nor do I think that this fact has ever been previously mentioned.

With regard to other mounds formed by stationary waves, I should suggest that the tidal sand ridges first discovered by Prof. Osborne Reynolds† in his model estuary were thus produced, and that the similar ridges to be found in natural estuaries, many of which Dr. Vaughan Cornish has so ably described and beautifully photographed, have a like origin.

Besides tidal ridges, it seems probable that the chains of sand banks in the sea and of sand dunes on shore, as well as the gigantic sand heaps in the Asiatic deserts described by Sven Hedin,‡ originate and grow under the action of waves that are stationary for longer or shorter periods, while the smaller ripples that cover all of them are due to vortices similar to those that I have shown to produce the ripple-mark of the sea-shore.

* "Rides Formées à la Surface du Sable Déposé au Fond de l'Eau," 'Archives des Sciences Physiques et Naturelles,' Période 3, vol. 9, p. 256 (1883).

† "First Report of Committee on the Action of Waves and Currents," 'Report of the British Association,' 1889.

‡ 'Central Asia and Tibet,' by Sven Hedin, vol. 1, pp. 248, 278.

The Absorption Spectra of Sulphur Vapour at Different Temperatures and Pressures and their Relation to the Molecular Complexity of this Element.

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[PLATE 5.]

This piece of work was undertaken at the suggestion of Prof. W. N. Hartley, who pointed out that it would be of interest to photograph the absorption spectra of sulphur vapour at temperatures corresponding to the two molecular masses S_8 and S_2 , the existence of which has been proved from vapour density determinations.

The absorption spectra of the vapour were photographed at temperatures varying from 530°C . up to 900°C . at atmospheric pressure, and at constant temperatures under pressures reduced down to about 10 mm. of mercury.

The results and their deductions may be briefly summarised as follows:—The photographs at constant pressure with the above variation of temperature show the presence of two distinct absorption spectra, which undoubtedly correspond to two definite molecular complexes. These two spectra are, from reasons stated later, attributed to the oscillations of the S_8 and S_2 molecular systems, the former producing, by taking up vibrations of certain frequencies, a series of absorption bands between frequency $n (= 1/\lambda)$ 2000 and n 2600 and having maximum absorption about n 2500, whilst the relatively lighter S_2 system, by taking up vibrations of greater frequencies, produces a series of bands lying between n 2900 and n 3820, with maximum absorption about n 3750. Moreover, since *only* two distinct spectra are evident, it is concluded that the equation $S_8 = 4 S_2$ represents the sole reaction that occurs in the dissociation of sulphur vapour on heating from its boiling point, 448°C ., up to about 900°C .

The interpretation of the photographs of the absorption spectra of the vapour at different (constant) temperatures, but with reduction of pressure, shows that above 580°C . the dissociation of the molecule S_8 is simple, that is to say, there is direct (and complete) dissociation into S_2 molecules, but at or below 520°C . the dissociation takes place with the formation of molecules intermediate in complexity between the above two aggregates.

The work of previous investigators* has shown that the absorption spectrum of sulphur vapour changes with variation of temperature. Thus, at the boiling point of the element, only the red end of the spectrum is transmitted (a thickness of 500 min. being examined), but if the temperature be raised, groups of dark bands are seen furrowing the violet and blue, the maximum intensity of each band being at the more refrangible side. All these observations were, however, made visually, and no mention is made of the approximate temperature (except when examined at the boiling point).

Experimental.—The sulphur vapour in the following series of experiments was examined in a vitreous silica tube with two approximately parallel sides, the thickness of the vapour being about 5 mm., since preliminary experiments had shown that, for varying temperatures, only a small thickness of sulphur vapour could be satisfactorily examined. To produce a tube of this description was at first a source of some difficulty; however, finally, the following method was employed and found to work satisfactorily:—A flat piece of graphite of the required thickness was placed inside a vitreous silica test-tube (special precautions being taken to free the latter from all basic matter), and the opposite sides of this were then blown flat against the graphite, using an oxy-hydrogen blow-pipe flame; a tube was thus formed having two walls practically parallel.

For the source of continuous rays, a spark passing between two metallic uranium electrodes, and condensed on the slit of the spectrograph by a cylindrical lens (a method devised by Prof. Hartley), was used in taking most of the photographs (see Plate 5), while a series of photographs was also taken with the vapour at varying temperatures, but constant pressure, using an ordinary acetylene flame. This flame gives a continuous spectrum, extending approximately to n 3000, being, however, greatly weakened from about n 2500.

For the plate of fig. 1, the test-tube, prepared in the manner described above, was fitted with (a) a small quartz tube sealed at one end and containing a thermocouple; (b) a second small tube to allow the excess of sulphur to escape.

Two to three grammes of pure recrystallised sulphur having been introduced into the apparatus, the latter was fixed in a horizontal position between the source of light and the cylindrical quartz lens. The rays from the spark (or acetylene flame, as the case was) thus passed through an approximately uniform thickness of sulphur vapour, and were then focussed on the slit of the spectrograph with the aid of the lens.

* Salet, 'Compt. Rend.,' 1871, vol. 73, pp. 559, 743; 1872, vol. 74, p. 865. Gernez, *ibid.*, 1872, vol. 74, p. 803. Lockyer, 'Roy. Soc. Proc.,' 1873—4, vol. 22, pp. 374—6.

The apparatus was heated by means of a large rectangular-shaped Mecke burner, the temperature of the sulphur vapour being varied by altering the position of the burner and regulating the height of the flame. The spectrograph, lens, etc., were protected from the strong heat of the flame by sheets of asbestos, a horizontal piece being placed just above the silica tube to deflect the heat downwards again, so that there might be the least possible difference in the temperature of the vapour in the upper and lower portions of the tube. The temperature was measured by means of a platinum-platinum-rhodium thermocouple, connected to a reflecting galvanometer, the deflection of the latter being noted at the commencement and end of the exposure at each different temperature; as the apparatus was heated up very slowly and carefully, the temperature remained practically constant during this period, the mean deflection, however, being taken.

The spectrograph employed had one Cornu's quartz prism of 60° , and lenses of 15-inch focus. The photographs were taken on 5×4 panchromatic (backed) plates, supplied by Messrs. Wratten and Wainwright.

The apparatus, etc., being arranged in the manner described, photographs of the absorption spectra of the sulphur vapour were taken at temperatures ranging from 530° C. up to 900° C., using the spark spectrum of uranium as the source of continuous rays. Fig. 1, Plate 5, is the reproduction of this series; thus, spectrum 2 of this figure is taken through the vapour at 530° C., spectrum 3 at 610° C., spectrum 4 at 770° C., spectrum 5 at 840° C., spectrum 6 at 870° C., and spectrum 7 at 900° C. On this figure only the portions of the spectra lying between n 2000 (or λ 5000) and n 3500 (λ 2860) are shown. A similar series was then taken, using the acetylene flame instead of the uranium spark, the temperature being varied from 490° up to 900° C.

The measurements of the spectra were made with a micrometer fitted with a travelling microscope* and capable of reading to $1/10,000$ th of an inch, and also by means of an ivory scale, graduated to $1/200$ th of an inch, but capable of being read to $1/500$ th of an inch with the aid of a lens. The latter method was found, on the whole, to be the more satisfactory of the two, as, owing to its high power, the microscope did not reveal some of the bands distinctly. Each spectrum was measured once with the micrometer and twice with the scale. These measurements were made in $1/100$ ths of an inch, and the corresponding wave-lengths ascertained from an interpolation curve (previously made for this spectrograph) on which measurements (in $1/100$ ths of an inch) of the principal lines of the cadmium,

* For more detailed description of this instrument, *vide* W. N. Hartley, 'Phil. Trans. Roy. Soc., A, vol. 208, p. 478.

lead, and tin spark spectra were plotted against their known wave-lengths (Ångström units). On each of the plates the spark spectrum of alloys of Cd, Pb, and Sn (not reproduced) was taken to check the measurements of the absorption spectra.

The bands observed all show a maximum absorption towards the more refrangible edge; the edges are not well defined, so that it is difficult to tell where the bands really commence and where they end; they are therefore described by measurements of the positions of maximum absorption in each case.

The width of the bands present in the visible region corresponds to about 25 Ångström units, that of the bands in the ultra-violet (about n 3750) to approximately 15 Ångström units. The maxima of absorption of the bands are stated in wave-lengths and also in oscillation frequencies (n); owing to the comparatively small dispersion employed, and the difficulty of determining exactly where the strongest absorption in the bands occurs, these measurements can only be relied on to within 5 or 10 Ångström units, according to the position of the bands. Again, in measuring some of the very faint bands, it was not always easy to tell whether certain weakenings of the spectra were due to absorption by the sulphur vapour or to the general diminution of intensity of the uranium spark spectrum. To decide this point, careful comparison of the absorption spectrum was made with a spark spectrum of uranium of practically the same intensity, and in this way the bands, whose wave-lengths are given later on, were shown to be undoubtedly due to the absorption by the sulphur vapour.

Turning to an examination of Plate 5, fig. 1, in spectra 2 and 3 it will be noticed that a series of bands occurs in the violet region, becoming apparently stronger in the more refrangible direction, until merged into complete absorption; thus, in spectra 2 and 3, there is complete absorption beyond n 2440. In the next spectrum (4), at 770° C., there is a marked change; at this temperature we still have the bands in the violet, with strong absorption beyond n 2425, but about n 2650 we get the spectrum again transmitted, extending to n 3170, whilst a second series of bands, starting about n 2850 and lying fairly close together, extends to the end of the spectrum. As the temperature is raised the absorption in the region n 2425 to n 2650 becomes weaker, being resolved into a series of bands, the maxima of any two consecutive bands differing, on an average, in oscillation frequency (n) by about 30, and finally, at 900° C., the spectrum is transmitted practically continuously over this region. The series of bands starting about n 2850 remains pronounced, extending further into the ultra-violet as the vapour diminishes in density (i.e. as the

temperature is raised). In No. 7 (*i.e.* at 900° C.) it is found that the spectrum is again faintly transmitted far down in the ultra-violet; that is to say, at this temperature we have practically continuous transmission as far as n 2850, then a series of bands, stretching as far as n 3330 (the absorption becoming stronger towards the more refrangible end of the spectrum), beyond this there is complete absorption as far as n 4270, but *from this point, however, there is faint continuous transmission to about n 4400.*

At relatively low temperatures, therefore (*i.e.* 500° to 700° C.), we have strong absorption in the blue and violet, stretching even for a short way into the ultra-violet, the mean position of maximum absorption being about n 2500. As the temperature is raised this absorption becomes resolved into a series of bands, the maximum absorption of the individual bands being in each case toward the more refrangible edge, and finally, at the highest temperature of the experiment (900° C.), these bands disappear almost entirely. At this temperature, however, the strong absorption in the ultra-violet is still evident, the mean position of maximum absorption being about n 3750. Other experiments at this temperature, with a relatively smaller thickness of vapour, indicate that this absorption is, in reality, composed of a series of bands (some of which, indeed, are shown on Plate 5, fig. 1, spectra 4 to 7), the maximum absorption of each of these bands being, as in the case of those occurring in the visible region, towards the more refrangible edge; these bands extend as far as n 3820, beyond which there is transmission of the continuous spectrum again, for a short distance further into the ultra-violet.

From these descriptions, it is evident that we must here be dealing with two distinct vibrating systems, which yield absorption spectra of great similarity, and which may conveniently be referred to as *A* and *B*, where—

A is that system existing in greater proportion at lower temperatures (*i.e.* 500° to 700° C.), and producing a series of absorption bands between n 2000 and n 2600, having a mean position of maximum absorption about n 2500, whilst—

B is that system which, coming more into evidence at higher temperatures (about 900° C.) produces by its vibrations a series of absorption bands similar in character to those produced by *A*, but extending from n 2850 to n 3820, with a mean position of maximum absorption about n 3750. (See fig. 4, Plate 5.)

At temperatures intermediate between 500° and 900° C., we thus have a mixture of the two spectra.

With an increase in the *number* of the oscillating systems *A* or *B*, the bands evident in the two regions of the spectrum mentioned become merged

into strong broad absorption bands; for example, at 770°C ., the number of systems *A* present, being greater than at the higher temperature 840°C ., the bands, evident in the spectrum at the latter temperature, become merged into strong absorption between $n\ 2425$ and $n\ 2650$ (*i.e.* between $\lambda\ 4125$ and $\lambda\ 3770$).

From the numerous investigations on the vapour density of sulphur,* the existence of the molecular aggregates S_8 and S_2 has been proved beyond dispute, the eight-atom complex occurring in greatest proportion about the boiling point of the element, whilst above 900°C . (and up to 1600°C .) the vapour is evidently composed solely of S_2 molecules.

There can be no doubt, therefore, that the absorption spectrum described as due to the vibrating system *B* is produced by the intra-molecular motions of the S_2 aggregates. The question then becomes, to what molecular complex may we assign the absorption spectrum produced by the system *A*? At the lowest temperature at which the vapour was examined in taking the plate for fig. 1 (*i.e.* 530°C .), the value for the vapour density lies between the figures corresponding to S_8 and S_6 respectively, approximating more nearly to the latter complex; accepting Biltz's figures at 534°C ., there must, however, be quite an appreciable proportion of S_8 molecules, even assuming that *no* S_2 aggregates are present. Now, if the series of absorption bands in the blue and violet be due to the vibrations of the S_6 systems, and since the series of bands in the ultra-violet is, without doubt, due to the presence of S_2 molecules, it seems perfectly legitimate to assume that the S_8 complex would produce absorption of some description in regions less refrangible than the blue, and that this absorption would diminish with rise of temperature. *No* such absorption, however, or change in absorption, has been observed between $n\ 2090$ and $n\ 1600$, when the temperature of the vapour was varied from 530°C . to 900°C . It seems reasonable, therefore, to attribute the two, and *only* two, distinct absorption spectra observed when sulphur vapour is heated from about 500°C . up to 900°C . to the presence of the two molecular complexes S_8 and S_2 .

From evidence of the absorption spectra, we must therefore come to the conclusion that, on heating sulphur from its boiling point up to 900°C ., there is direct dissociation of S_8 into S_2 molecules, without the production of complexes (such as S_6 or S_4) intermediate in size between the above-mentioned aggregates.

It will thus be seen that these results verify the conclusions of Biltz, who,

* Deville and Troost, 'Compt. Rend.,' vol. 56, p. 891. Biltz, 'Ber.,' 1888, vol. 21, pp. 2013—2017. Bleier and Kohn, 'Monatsh.,' 1899, vol. 20, p. 505. Biltz, 'Ber.,' 1901, vol. 34, p. 2490. Bleier and Kohn, 'Ber.,' 1900, vol. 33, p. 50. Bleier and Kohn, 'Monatsh.,' 1900, vol. 21, p. 575, etc.

from the course of the curve connecting the vapour density of this element with rise of temperature, felt justified in making the following statement:—"Demnach besitzt der Schwefel nur zweierlei Molekeln, nämlich Molekeln S_8 , und zwar im gelösten Zustande, und ferner Molekeln S_2 , die rein im Schwefelgase oberhalb 850° , und mit Molekeln S_8 gemischt im Schwefelgase bei niedriger Temperatur vorliegen" ('Ber.,' 1901, vol. 34, p. 2495).

*The Absorption Spectra of Sulphur Vapour at Different (Constant)
Temperatures, under Reduced Pressures.*

Having arrived at the conclusions already stated, for the dissociation of the S_8 molecule under the action of heat, at constant pressure, it seemed advisable to examine the change produced in the absorption spectrum under reduced pressures, but at constant temperatures, in order to ascertain, if possible, whether under these conditions there is evidence of the existence of molecules other than the S_8 and S_2 complexes. This part of the work was especially desirable, since it has been shown by G. Preuner, from examination of the isotherms of dissociation of sulphur vapour at different temperatures, that the presence of molecules intermediate in size between S_8 and S_2 is highly probable. The deductions of Preuner,* from the isotherm of dissociation at 448° C., point to the occurrence of S_8 , S_6 , S_4 , and S_2 molecules, but lately this author, in conjunction with W. Schupp,† has come to the conclusion that only the complexes S_8 , S_6 , and S_2 are present during the dissociation produced by reduction of pressure, at temperatures between 300° C. and 850° C.

Experimental.—For these experiments another silica test-tube was flattened in the manner already described. This tube was fitted with a rubber bung, through which passed (a) a closed tube holding the thermocouple; (b) the exit tube, through which the apparatus was exhausted. Some asbestos fibre was wrapped round the tube containing the thermocouple, in a position just above the point where the test-tube had been flattened, in order to prevent the molten sulphur condensed in the upper portion of the tube from running down the parallel faces, and thus preventing free transmission of the light. The rubber bung was wired into the tube, after introducing the sulphur, and on testing, the apparatus was proved to be gas-tight.

The tube was fixed in a vertical position between the uranium spark and the cylindrical focussing lens, the exit tube (b) being connected to a Töpler evacuating pump; the silica tube passed through two horizontal sheets of

* Preuner, 'Zeit. Phys. Chem.,' 1903, vol. 44, p. 732.

† Preuner and Schupp, 'Zeit. Phys. Chem.,' 1909, vol. 68, p. 129.

asbestos, in order to keep the upper portion as cool as possible, while the lower, flattened portion remained at a constant temperature.

In taking the plate for fig. 2, a horizontal Mecke burner was used for heating purposes, the temperature of the vapour remaining constant at 580° C.

In the series reproduced in figs. 2 and 3 the pressure was gradually reduced from atmospheric down to about 10 mm., photographs being taken at different intermediate pressures.

To obtain the photographs in fig. 3, *i.e.* with sulphur at 450° C., it was found necessary to place the tube containing the sulphur in a small heating apparatus, composed of two vertical curved copper cells, mounted on a flat piece of copper, and containing an alloy of aluminium and zinc (melting about 600° C.), the two cells being sufficiently far apart to allow the passage of light through the silica tube containing the sulphur vapour. This cell was heated from underneath by means of a large Mecke burner, and in this way it was found possible to keep the vapour at a constant temperature, which however, could be varied by regulating the Mecke burner.

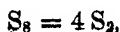
It was found that different pieces of silica apparatus varied in their capability of transmission of light. Thus the tube used in the case of fig. 1 was found to be very transparent (see spectrum 1, fig. 1), whilst that used in the experiments under reduced pressure (figs. 2 and 3) was found to exert rather a considerable general weakening of the spectrum (compare spectra 1 and 2 on fig. 2, spectrum 1 being the uranium spark spectrum, spectrum 2 the same after passing through the silica tube, the same period of exposure (30 seconds) being given in each case). The fact that the spectra exhibited on the plates of figs. 2 and 3 were much weaker than those on the first plate is attributed to this absorption by the silica apparatus.

Fig. 2 shows the effect of reduction of pressure at 580° C., the series of photographs being taken through 4½ mm. of sulphur vapour, the pressure varying from atmospheric (756 mm.) down to 25 mm. In this figure spectrum 3 shows the absorption at 756 mm., spectrum 4 that at 691 mm., spectrum 5 at 616 mm., and so on, the pressure being gradually reduced to 25 mm. (spectrum 10).

A glance at the reproduction of this plate shows the similarity to fig. 1. Thus spectrum 3 is altogether cut off about n 2325, spectrum 4 is cut off about n 2380, then there is absorption as far as n 2715, but from this point we have the spectrum again transmitted to n 3095, beyond which there is complete absorption. In this spectrum bands are present in the violet region coinciding in position with those previously measured on the plate of fig. 1. In the next spectrum (5) the bands in this region are still evident,

whilst bands are to be seen in the ultra-violet, starting about n 3040. As the pressure is reduced the absorption in the violet region becomes less, whilst the series of bands beyond n 3040 becomes more pronounced, extending further into the ultra-violet, until at a pressure of 272 mm. (spectrum 8) there is continuous transmission as far as n 3040, then the series of bands mentioned above, the spectrum being cut off about n 3420. As the pressure is still further reduced, more of the spectrum is transmitted, until at 25 mm. there is continuous transmission as far as n 3040, then a series of bands occurs (the maximum absorption of each band being, as in the series shown in fig. 1, towards the more refrangible edge, whilst from the measurements of the spectra the maxima of these bands were found to have the same wave-lengths as those measured in fig. 1, in the corresponding region of the spectrum, and previously attributed to the presence of S_2 molecules). The absorption becomes stronger towards the more refrangible end, until about n 3580 there is complete absorption, stretching to approximately n 4130, from which point, however, as far as n 4400 there is faint continuous transmission. (NOTE.—The change in the absorption spectrum on fig. 2 is roughly outlined, in order that the variation of absorption may be more evident, whilst some of the bands are dotted, in order to indicate their positions more clearly.)

A careful comparison of figs. 1 and 2, with reference to the measurements of the absorption bands, positions of maximum absorption, etc., makes it evident that here we are dealing with a case of dissociation, similar in every respect to that taking place when sulphur is heated from its boiling point up to 900° C. at constant pressure. In other words, *the dissociation of the sulphur molecules at a temperature of 580° C., and produced by reduction of pressure, evidently takes place according to the equation*



without the formation of molecules intermediate in complexity.

Other series of photographs showing the variation in the absorption spectrum of the vapour with reduction of pressure, whilst at constant temperatures, were then taken; thus photographs were taken showing the effect at temperatures of 450° (fig. 3) and 380° C. respectively (the latter plate not being reproduced).

A comparison of the series in fig. 3 with figs. 1 and 2 shows at first glance that here we must evidently be dealing with a case of dissociation different in the extreme to that already described.

There is, under these conditions of temperature and pressure, no evidence of any band or bands in the violet region, the only effect of reduction of

pressure being to cause an extension of the spectrum towards the more refrangible end, until pressures below 90 mm. are reached, when it is seen that bands begin to appear in the ultra-violet. Thus, in spectrum 8 we have a series of bands starting about n 3340 and extending to n 3530, where the spectrum has become exceedingly weak, and beyond which there is complete absorption. As the pressure is further reduced, these bands extend for a greater distance into the ultra-violet, until at 11 mm. (spectrum 10) the bands are evident to about n 3820, beyond which point the continuous spectrum is again faintly transmitted, being finally cut off about n 3870. The wave-lengths of the maxima of these bands were found to agree with the figures for the bands occurring in fig. 2, spectra 9 and 10, and which have been attributed to the intra-molecular motions of the S_8 complexes. At the temperature of 380°C. , a similar effect was produced on the absorption spectrum by reduction of pressure, bands being present at pressures below 80 mm., coinciding in position with those measured on fig. 3 in the ultra-violet.

A similar set of photographs through the vapour at a temperature between 450° and 580° was then taken; this showed a series of absorption spectra when the temperature of the sulphur remained constant at 520°C. It was evident from a study of this plate that at the latter temperature the course of dissociation, as interpreted by change in the absorption spectrum, is similar to that taking place at the lower temperatures.

Let us suppose, for the moment, that molecular complexes such as S_8 and S_4 exist; from what has previously been said concerning the connection between the absorption spectra attributed to the S_8 and S_2 molecules, one would expect that absorption spectra similar in character to the two types already observed and assigned to these two molecules would be produced by aggregates such as S_6 and S_4 . That is, for the S_8 molecules we might expect a series of absorption bands having strongest absorption somewhere about n 2800, and for the S_4 molecules a series of bands with maximum absorption about n 3200 (the mean position of maximum absorption for the S_8 and S_2 aggregates being, as already pointed out, at n 2500 and n 3750 respectively).

Suppose now we have a gaseous mixture composed of the four sets of molecules, S_8 , S_6 , S_4 , S_2 , the most probable effect on the absorption spectrum of the vapour would be that bands similar to those measured on figs. 1 and 2 in regions less refrangible than n 3200 would not be seen distinctly, owing to the overlapping of the four different spectra, due to the intra-molecular vibrations of S_8 , S_6 , S_4 , and S_2 complexes, but a general weakening of the spectrum might be expected from about n 2300 (or further towards the ultra-

violet, depending on the concentration of the S_8 molecules in the mixture). On referring again to the spectra in fig. 3, it will be noticed that in this series in *no case* does the spectrum appear sharply cut off, but there is distinct evidence of a *weakening* from a certain region to the end of the spectrum; thus in fig. 3, spectrum 3, a gradual weakening is noticeable from about n 2350 to the end of the spectrum at n 2570. Similarly in the other spectra a corresponding weakening is evident, whilst by comparison of fig. 3 with fig. 1 the difference between the sharp cutting off of the spectra on the latter and the shading off of the spectra on the former figure is clearly shown.

The obvious conclusion to be deduced from these results is that *molecules intermediate in size between the eight-atom complex and that containing two atoms are formed as products of the dissociation of the S_8 complexes, when this takes place at temperatures below 520°C. , whereas at 580°C. (and above) the equation $S_8 = 4 S_2$ evidently expresses the sole reaction that occurs.*

It will thus be seen that results obtained from a purely spectroscopic source give independent evidence in confirmation of the thermodynamic deductions of G. Preuner,* given in 1903, in explanation of the course of dissociation of sulphur vapour at 448°C. ; the recent conclusions, however, arrived at by this investigator (in collaboration with W. Schupp)†, from the isotherms of dissociation of the vapour at temperatures above 550°C. do not appear to be in agreement with the interpretation given in this paper of the changes produced in the absorption spectrum of sulphur vapour at 580° by reduction of pressure.

A plate, which has not been reproduced, was taken especially for the red end of the spectrum, employing the acetylene flame. On this plate a few weak bands, lying in the blue and indigo, were measured, which were not evident on the plate of fig. 1. These bands gradually disappeared as the temperature was raised, vanishing altogether above 870°C.

The following were the wave-lengths of these bands:—4775, 4705, 4645, 4580, 4530, 4465, 4405, 4350. In addition, the bands measured on the plate of fig. 1, in the violet, were also evident on this plate.

It has been already pointed out that the bands lying between n 2000 (λ 5000) and n 2600 (λ 3846), (measured on the plates of figs. 1 and 2), may be attributed to the presence of the S_8 molecules, whilst those occurring beyond n 2920 in the more refrangible direction are due to S_2 molecules.

These results may be summarised in the following tables:—

* Preuner, 'Zeit. Phys. Chem.,' 1903, vol. 44, p. 733.

† Preuner and Schupp, 'Zeit. Phys. Chem.,' 1909, vol. 68, p. 129.

A. Bands due to S_8 Molecules.

Position of maximum absorption.		Remarks.
λ .	$n (= 1/\lambda)$.	
4775	2094	<p>The maxima of these bands appear to be, in every case, towards the more refrangible edge of the band (this fact being previously noted by Salet* for the <i>visible region</i>).</p> <p>The strongest bands occur about n 2500.</p>
4705	2125	
4645	2153	
4580	2183	
4530	2207	
4465	2239	
4405	2270	
4350	2299	
4290	2331	
4245	2356	
4195	2384	
4150	2410	
4100	2439	
4050	2469	
4005	2497	
3985	2509	

* 'Compt. Rend.,' 1872, vol. 74, p. 865.

B. Bands due to S_2 Molecules.

Position of maximum absorption.		Remarks.
λ .	$n (= 1/\lambda)$.	
3415	2928	<p>All these bands are in the ultra-violet.</p> <p>The maxima of absorption of these bands are towards the more refrangible edge of the band in each case.</p> <p>The strongest bands (maximum absorption) occur about n 3750.</p>
3365	2972	
3330	3003	
3290	3039	
3255	3072	
3215	3110	
3170	3155	
3130	3195	
3095	3231	
3060	3268	
3025	3306	
2990	3344	
2960	3378	
2930	3413	
2900	3448	
2860	3496	
2835	3527	
2805	3565	
2770	3610	
2745	3648	
2715	3688	
2690	3717	
2665	3752	
2640	3788	
2620	3817	

These tables contain what are believed to be the principal bands due to the molecular complexes S_8 and S_2 , but there is no intention of implying that they are the *only* bands due to these two molecules.

It is interesting to note that the difference in wave-length between the two extreme bands of each series is approximately the same in both cases. Thus, in Series A, the first and last bands, given above, differ by 790 Ångström units; whilst in Series B there is a difference of 795 Ångström units.

The two series of bands, A and B, are shown on Plate 5, fig. 4, mapped in oscillation frequencies, the black lines and shading indicating absorption. The position of maximum absorption of each band is towards the more refrangible edge, whilst the individual bands of each series appear to become stronger also in the more refrangible direction. When mapped in this fashion, the similarity between the two series becomes more evident.

Apologies must be made for the reproductions, which in several cases do not bring out portions of the spectra, bands, etc., that were clearly shown on the original plates. Above portions of certain of the spectra, horizontal lines have been drawn to indicate the presence of the continuous spectrum transmitted beyond n 3820, whilst some of the bands are indicated by dots. An approximate scale of oscillation frequencies has been affixed to each plate.

It is hoped to repeat these experiments shortly, employing much greater dispersion, in order that the bands given by the sulphur vapour may be further examined, and more accurate determinations made of their wave-lengths and oscillation frequencies. With finer measurements, attempts will be made to see whether these bands conform to any law similar to that given by Deslandres* for the band spectrum of nitrogen.

In conclusion, I have to thank Prof. Hartley for his kindness in giving me many fruitful suggestions, and also for the trouble he has taken in the revision of this paper.

* 'Compt. Rend.,' 1902, vol. 134, pp. 747—750.

DESCRIPTION OF PLATE.

Fig. 1.—Series taken at constant *pressure*, 742 mm. Thickness of sulphur vapour, $5\frac{1}{2}$ mm.

Spect. 1.—Spark spectrum of uranium through empty silica tube.

2.—Same through sulphur vapour at 530° C.*

3.— " " 610°

4.— " " 770°

5.— " " 840°

6.— " " 870°

7.— " " 900°

Lengths of Exposure.—Spectrum 1, 30 seconds; spectra 2—7 (inclusive), 1 minute.

Fig. 2.—Series taken at constant *temperature*, 580° C. Thickness of sulphur vapour, $4\frac{1}{2}$ mm.

Spect. 1.—Spark spectrum of uranium.

2.—Same through empty silica apparatus.

3.— " sulphur vapour (580° C.), press. 756 mm.

4.— " " " 691 "

5.— " " " 616 "

6.— " " " 500 "

7.— " " " 386 "

8.— " " " 272 "

9.— " " " 168 "

10.— " " " 25 "

11.—Spark spectrum of uranium.

Lengths of Exposure.—Spectra 1, 2 and 11, 30 seconds; spectra 3—10 (inclusive), 1 minute.

Fig. 3.—Series at constant *temperature*, 450° C. Uranium spark spectrum through sulphur vapour at 450° C.; thickness, 4 mm.

Spect. 1.—Press. 770 mm.

Spect. 6.—Press. 229 mm.

2.— " 639 "

7.— " 91 "

3.— " 558 "

8.— " 36 "

4.— " 462 "

9.— " 21 "

5.— " 350 "

10.— " 11 "

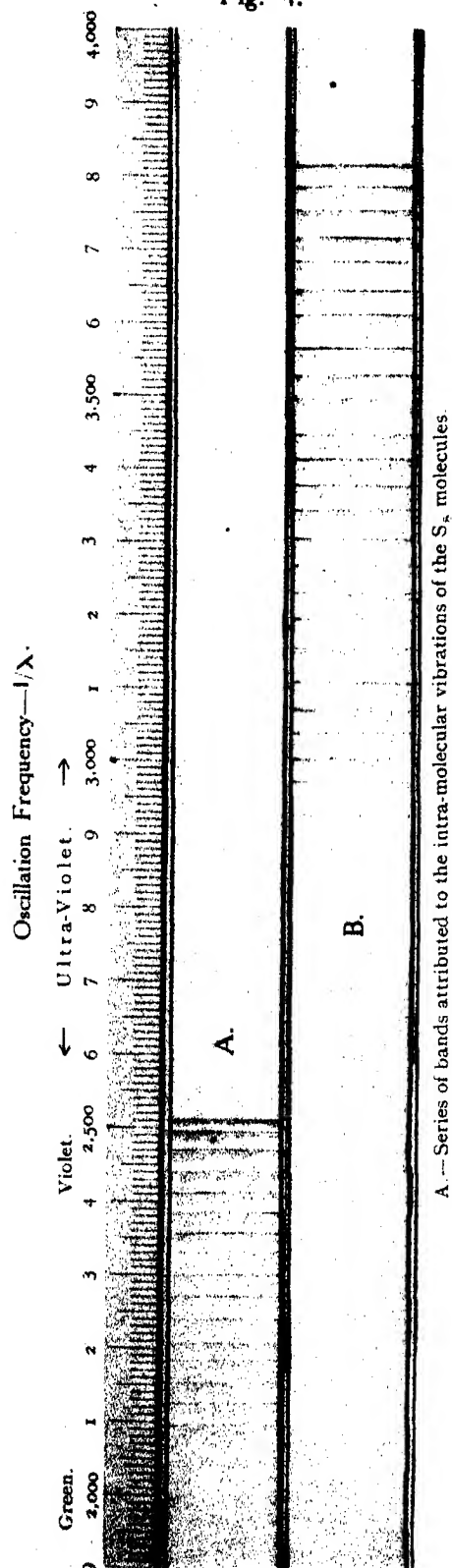
11.—Uranium spark spectrum through empty silica apparatus.

Lengths of Exposure.—Spectra 1—10 (inclusive), 1 minute; spectrum 11, 30 seconds.

Fig. 4.—Diagram of oscillation frequencies of two series of bands, A and B.

* The exposure at this temperature (530° C.) was slightly longer than at the others, with the result that rays up to n 2440 are shown, whilst at the next higher temperature the spectrum is not evident beyond n 2425.

Fig. 4.



A. — Series of bands attributed to the intra-molecular vibrations of the S_8 molecules.

B. —

Fig. 1.

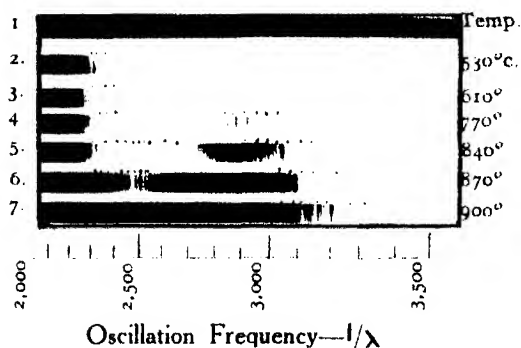


Fig. 2.

Temperature of Vapour = 580°C.

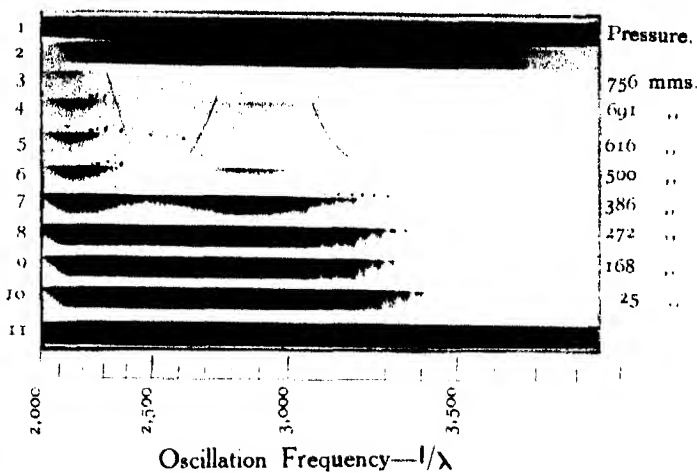
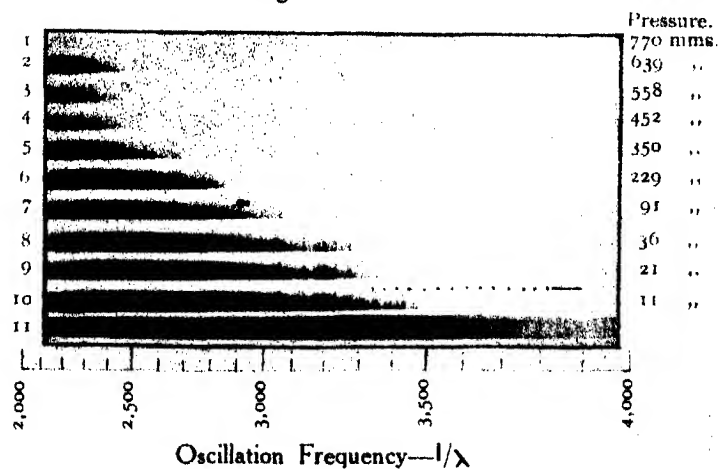


Fig. 3.

Temperature of Vapour = 450°C.



*A Determination of the Ratio of Mass to Weight for a
Radioactive Substance.*

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(Communicated by Sir J. J. Thomson, F.R.S. Received June 20,—
Read June 30, 1910.)

Experiments have been made from time to time by different observers, with a view of testing the constancy of the ratio of mass to weight for various substances. Their results have been uniformly negative so far as indicating any deviation from constancy is concerned. Several years ago an experiment of this nature was undertaken by Prof. Sir J. J. Thomson, who used a pendulum the bob of which was made of radium. The quantity of radium, however, was small, and it was found to be impossible to obtain a very high degree of accuracy. The considerations which led to the supposition that radium might differ from non-radioactive substances in the above respect were as follows:—*

“The simplest electrical system we know, an electrified sphere, has attached to it a mass of ether proportional to its potential energy, and such that if the mass were to move with the velocity of light its kinetic energy would equal the electrostatic potential energy of the particle. This result can be extended to any electrified system, and it can be shown that such a system binds a mass of the ether proportional to its potential energy. Thus a part of the mass of any system is proportional to the potential energy of the system.

“The question now arises, Does this part of the mass add anything to the weight of the body? If the ether were not subject to gravitational attraction it certainly would not, and even if the ether were ponderable we might expect that as the mass is swimming in a sea of ether it would not increase the weight of the body to which it is attached. But if it does not, then a body with a large amount of potential energy may have an appreciable amount of its mass in a form which does not increase its weight, and thus the weight of a given mass of it may be less than that of an equal mass of some substance with a smaller amount of potential energy. Thus the weights of equal masses of these substances would be different.

“The radioactive substances are constantly giving out large quantities of heat, presumably at the expense of their potential energy; thus, when these substances reach their final non-radioactive state their potential energy must

* Prof. Sir J. J. Thomson, Presidential Address, British Association, Winnipeg, 1909.

be less than when they were radioactive. Prof. Rutherford's measurements show that the energy emitted by 1 gramme of radium in the course of its degradation to non-radioactive forms is equal to the kinetic energy of a mass of $\frac{1}{13}$ milligramme moving with the velocity of light.

"This energy, according to the rule I have stated, corresponds to a mass of $\frac{1}{13}$ milligramme of the ether, and thus a gramme of radium in its radioactive state must have at least $\frac{1}{13}$ milligramme more of ether attached to it than when it has been degraded into the non-radioactive forms. Thus, if this ether does not increase the weight of the radium, the ratio of mass to weight for radium would be greater by about 1 part in 13,000 than for its non-radioactive products."

These considerations also apply to uranium, for "we have got good reason for supposing that uranium is a parent of radium, so that the great potential energy and large ethereal mass possessed by the radium will be also in the uranium."

In the present paper some experiments made with uranium oxide are described. The results, however, show that the ratio of mass to weight of this substance does not differ appreciably from that of the non-radioactive substance with which it was compared. The paper is divided into the following sections:—

1. Preliminary experiments with a wire pendulum.
2. Theory of a new rigid pendulum.
3. Description of the apparatus.
4. Method of experiment.
5. Experimental results.
6. Conclusion.

1. *Preliminary Experiments with a Wire Pendulum.*

A pendulum based on the principle employed by Bessel in his investigations on the value of g for various substances was constructed for Prof. Thomson by the Cambridge Scientific Instrument Company, and observations were made upon it by the writer at Prof. Thomson's request. Although sufficiently accurate results were not obtained with this apparatus, it may be briefly described, as it was of great service in shaping the subsequent course of the investigation. It consisted of a hollow cylindrical bob of aluminium, which could be suspended by a wire from a knife-edge by means of a suitable attachment. Either of two wires, of lengths 75 and 150 cm. respectively, could be used. The method of experiment was as follows:—The bob was filled with red lead and suspended by means of the long wire and the

time of swing determined. Then the short wire was substituted for the long one and the time again observed. The red lead was then replaced by uranium oxide, and the times taken as before. The pendulums approximate to simple pendulums. Assuming them to be actually simple, and writing t_1, t_2 , for the times of the long and short pendulums respectively and l_1, l_2 , for the lengths when the first substance, for which the acceleration of gravity is g , is employed, and the same letters dashed for the corresponding quantities for the second substance, we have

$$t_1^2 - t_2^2 = \frac{4\pi^2}{g}(l_1 - l_2), \quad t_1'^2 - t_2'^2 = \frac{4\pi^2}{g'}(l_1' - l_2').$$

But $l_1 - l_2 = l_1' - l_2' =$ difference in the lengths of the wires irrespective of the absolute lengths, and therefore

$$\frac{t_1^2 - t_2^2}{t_1'^2 - t_2'^2} = \frac{g'}{g},$$

so that the ratio of the values of g is deduced from the times alone. In the actual case, since the pendulums are not simple, it is necessary to know approximately the distance of the centre of gravity from the knife-edge in each case, as well as the other dimensions of the apparatus, but slight errors in the packing of the bob, with corresponding displacements of the centre of gravity of the substance, will have but little influence on the accuracy of the experiments.

After many experiments had been made with this apparatus, and considerable experience gained on minor points, it was discarded, mainly because it was found to be impossible to fit together the different parts of the pendulum always in exactly the same way, so as to give sufficiently consistent results. Thus differences of 1 in 10,000 or 20,000 frequently occurred in the time of swing after all other errors which could be detected had been as far as possible eliminated. In view of this, it appeared desirable to the writer to construct a rigid pendulum with two knife-edges permanently fixed to it, and to employ some kind of lifting apparatus by means of which the change from one knife-edge to the other could be made without in any way handling the pendulum, or opening the case in which it was enclosed. Such an apparatus was constructed in the laboratory workshop to the writer's designs, and a standard invar pendulum was supplied by the Scientific Instrument Company for the purpose of checking the clock which was used in the experiments, as the rate of this had been found to be somewhat variable.

The theory given above is of course inapplicable to the new pendulum, but a method of exhibiting the results in a simple manner will be given in the next section. The only drawback in the use of a rigid pendulum is that

there is considerable non-effective mass, but this is quite outweighed by the advantages gained.

2. *Theory of a New Rigid Pendulum.*

The pendulum consists of a rigid rod AA (fig. 1), having two knife-edges fixed at the places shown in the figure, and a hollow cylindrical bob B which can be filled with either of the substances to be experimented on. The bob is not permanently fixed, but can be moved through a small range up and down the rod. By means of suitable arrangements the time of swing can be taken first about one of the knife-edges and then about the other, the position of the bob remaining unaltered.

Considering the time of swing about one of the knife-edges, we have $t = 2\pi\sqrt{(I/Mgh)}$, where I is the moment of inertia about the knife-edge, Mg the total weight of the pendulum, and h the distance of the centre of gravity from the knife-edge. We shall assume that gravity does not change during the course of the experiments, but g may be different for the different substances used. The total weight, however, of the pendulum remains constant through all the experiments, for the weight of the bob is always carefully adjusted by means of a balance after being filled. The balance of course ensures equality of weights and not of masses, the ordinary use of the balance for the determination of masses depending on the supposed invariability of g for the substances employed. Since therefore in the case of uranium we know neither mass nor acceleration of gravity, but only weight, it will be convenient to write the expression for the time $t = 2\pi\sqrt{(I/Wh)}$ where W is a constant and is the total weight of the pendulum. Variations of mass will only affect the moment of inertia in this expression. It is impossible to fill the bob so uniformly that the centre of gravity shall always be exactly at the same point, but it will be seen that errors due to this can be rendered unimportant by the method to be explained. We will first, however, assume that the bob is uniformly packed, and that a normal substance is used so that g has its ordinary value throughout the pendulum.

It is possible to find a point X, say, on the rod about which the time of swing of the pendulum is independent of small changes in the position of the bob.

In practice, the knife-edges are fixed one above the point X and one below it.

The time of swing of the pendulum about a point of the rod above X will be increased by a slight lowering of the bob. The time of swing about a point below X will be diminished by the lowering of the bob. Let t_1, t_1' , be the times about the upper and lower points respectively, the bob being in its

first position, and t_2, t_2' , the times with the bob lowered. Then $t_2 > t_1$ and $t_2' < t_1'$. This is shown on the accompanying small diagram A, in which the ordinates represent times from the upper point and abscissæ times from the lower point.

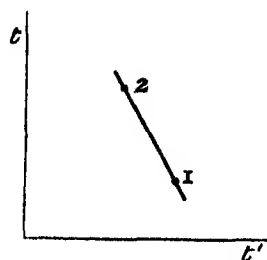


DIAGRAM A.

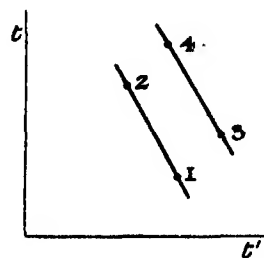


DIAGRAM B.

Points corresponding to other positions of the bob will lie on the line 1, 2, which will be nearly straight if the displacements are very small. This line will be called the *characteristic line* of the pendulum for the given points of suspension.

We will now return to the expression for the time of swing,

$$t = 2\pi\sqrt{(I/Wh)},$$

and suppose it to apply to one of the observations on the diagram. Suppose the mass of the bob to be increased by the use of another substance, the weight remaining unaltered. Now I will be increased, and therefore t will be greater than before. This is true whatever point of suspension be used. If the bob be replaced in exactly the same position as it was when point 1 was taken, and the new packing be exactly uniform, the new point, 3 say, will be higher up the diagram than 1, and also more to the right, both its co-ordinates having been increased in magnitude (see small diagram B).

If the bob be now moved down to the position which it occupied when point 2 was determined, a new point 4 will be obtained on the line through 3 approximately parallel to 1, 2. Thus the pendulum will have a new characteristic line nearly parallel to the old one. In order, therefore, to find out whether equal weights of different substances possess different masses, it is only necessary to plot a few points on the diagram for different positions of the bob for each substance, and to draw the characteristic lines. If the masses are different, the lines will be separated; if not, they will coincide. Accidental variations of the height of the centre of gravity of the bob, due to inequalities of packing, merely cause displacements of the points along the characteristic lines, and are therefore of no consequence.

It is necessary, however, to exercise care in packing, as otherwise irregu-

larities in the moment of inertia of the bob about an axis through its centre of gravity parallel to the knife-edges may be sufficiently large to influence the final results. They have been rendered unimportant by the method of packing described in section 4.

Errors in weighing the bob also require consideration. This will be given later, and it will appear that they also are unimportant.

Corrections for changes of temperature of the pendulum and changes of the density of the air will be required. As the experiment is not intended to give absolute, but only relative, results, it will not be necessary to reduce to zero of temperature and density, and therefore we shall only consider deviations from the mean conditions. Thus the corrections will be small, and an approximate investigation of them will suffice.

As regards temperature of the pendulum, it will be sufficient to assume that the whole expands uniformly with rise of temperature. Let α = coefficient of linear expansion at θ° , then the time of swing at $\theta + 1$ will be t_1 , where

$$t_1 = 2\pi \sqrt{\frac{l(1+\alpha)}{Wh(1+\alpha)}} = t\sqrt{1+\alpha} = t + \frac{1}{2}\alpha t.$$

Thus for a rise of one degree we reduced the observed result by $\frac{1}{2}\alpha t$, where t is the time at the standard temperature θ .

With regard to the effect of changes in the density of the air, we need only consider buoyancy and the mass of air carried along with the pendulum. This latter consists of two parts, namely, that which surrounds the pendulum and moves with it, and that within the hollow bob (which is not air-tight) between the particles of the substance therein contained. Some air will pass in and out of the bob as the conditions change. We shall calculate the buoyancy as affecting the whole volume of the bob, as well as the rest of the pendulum, and therefore any air which enters the bob must be considered to add its weight to the bob as well as its mass. We thus have to apply corrections for—

- (1) A variation in the weight of the moving system, equal to the variation in the weight of the air displaced by the whole pendulum, and acting at the centre of gravity of this displaced air.
- (2) A variation in the moment of inertia of the system, equal to that in the air carried along around the pendulum.
- (3) A variation in the weight of the bob, equal to the variation in the weight of the enclosed air.
- (4) A variation in the moment of inertia of the bob, equal to the variation in that of the enclosed air.

The standard invar pendulum is also subject to corrections (1) and (2). The effect of this is to partially eliminate the corrections, and in view of this it will be allowable to make the assumption that the mass of air carried along with each pendulum is equal to the mass displaced. With regard to corrections (3) and (4), it will be assumed that the density of the air inside the bob is equal to that outside. The corrections will be considered in detail in a later section of the paper.

3. *Description of the Apparatus.*

The main apparatus is shown generally in fig. 1, and an enlarged portion in profile in fig. 2. The same letters are used for corresponding parts in the two figures. A, A represents the rod of the experimental pendulum, B is the bob, C, C the cast-iron supporting bracket, which is slotted at D, D and which carries slotted plates, E, E, which can be levelled, and to which are fixed agate planes, F, F, on which the knife-edges of the pendulum bear. The upper plate is thrown back 1 cm., as shown in fig. 2. The pendulum is there shown with the upper knife-edge in contact with its agate planes, and in this position the lower knife-edge is free. On the other hand, when the lower knife-edge is in position the upper one swings clear of its planes. This change of position is accomplished by means of the lifting apparatus shown in the figures. Two pairs of brackets, G, G, are attached to a flat rod, H (this lies exactly behind the pendulum rod in fig. 1), which is moved in its own plane by eccentrics, J, J, so that any point in it describes a part of a circle whose radius is 5 mms. This throw is slightly exaggerated in fig. 2 for the sake of clearness. The arms, G, G, have V-shaped grooves, in which pins, L, L, are seen lying in fig. 2. These pins are fixed to the pendulum, and by means of them the arms, G, G, lift the pendulum and carry it over from the position shown in fig. 2 to that in which the lower knife-edge engages with its agates. The arms then continue their motion slightly, so as to release the pins, L, L, and allow the pendulum to swing clear of its supports. The eccentrics are actuated by rods, cranks, and connecting rod, as shown at M, M, in fig. 1. These pass outside the case in which the pendulum is enclosed, so that the change from one knife-edge to the other can be effected without opening the case. This is an important point in experiments of this nature. A mirror is fixed to the pendulum at N, and another one, P, which remains stationary during an observation, is attached to an adjustable support Q. This has two motions controlled by rods which pass through the case at R. The bracket carrying this fixed mirror arrangement is shown at S. A bracket with two screws is shown at T, near the bob in fig. 1. The screws are adjusted so as to very nearly touch the rod whenever the bob is removed for refilling or

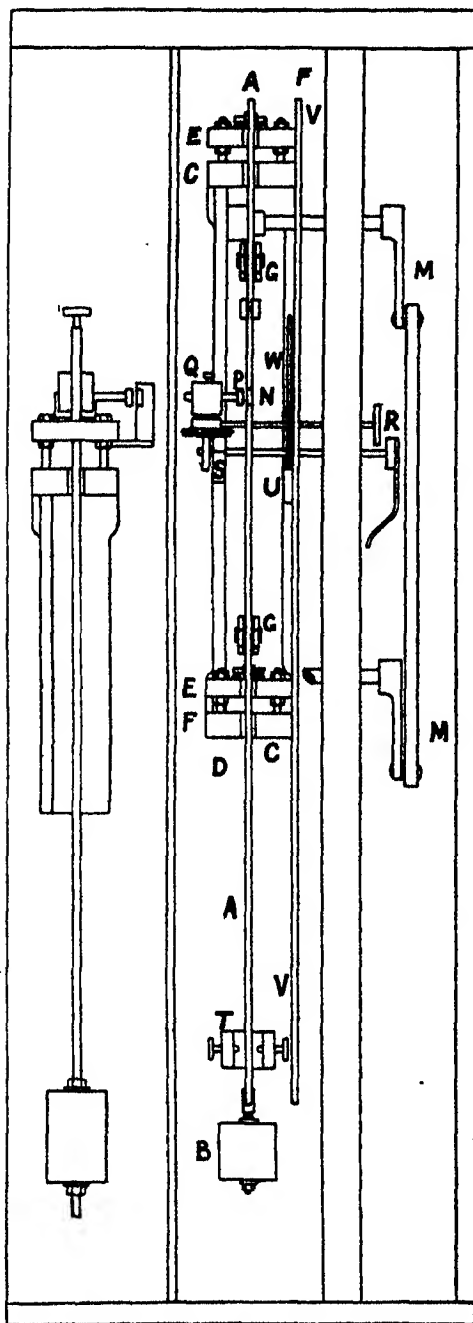


FIG. 1.

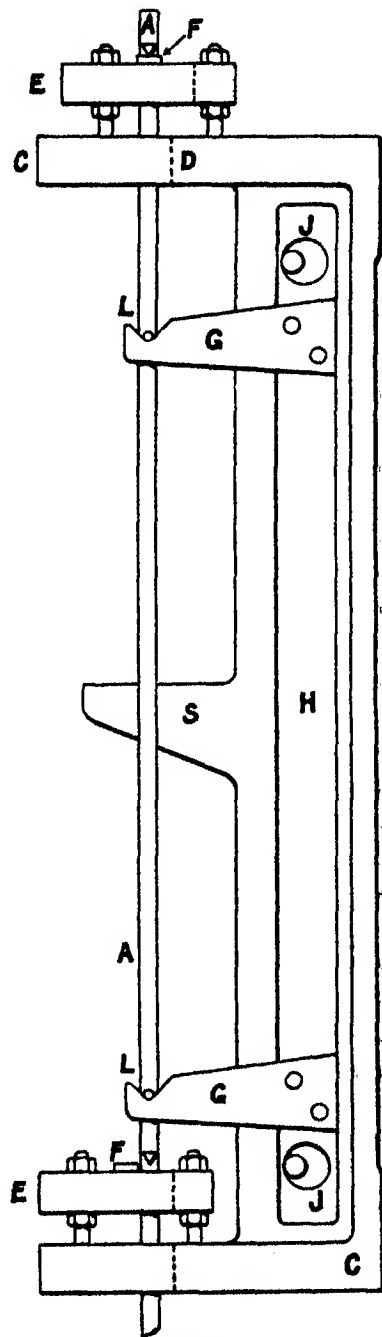


FIG. 2.

replaced. They are for the purpose of steadying the rod, and are screwed out of the way when the bob is in position. VV is a rod similar to the pendulum rod. It has a brass projection U, which is drilled to receive the bulb of a thermometer W. The reading of this thermometer is taken as indicating with sufficient accuracy the temperature of the pendulum rod. A thermometer is also suspended in the case to indicate the temperature of the air.

The standard invariable pendulum, to which all observations are finally referred, is shown to the left of the experimental pendulum, in fig. 1. The rod is of invar, and the bob of brass. It is provided with mirrors, similar to those of the other pendulum.

The pendulums are set up in a niche in the wall of one of the rooms on the ground floor of the new buildings of the Cavendish Laboratory. The cast-iron brackets are bolted to the wall which forms the back of the niche. Double partitions of wood, packed with sawdust, are fixed above and to the right of the pendulums, and the front is closed with two doors similarly made, an upper and a lower door. The lower one can be opened independently, when it is necessary to remove and replace the bob. A plate glass window is fixed in the upper door opposite the mirrors. This is closed by a shutter, except when observations are being made. There is also a partition between the two pendulums. No difficulty was anticipated, nor has any been experienced, due to the fact that both pendulums are fixed to the same wall. Their periods are quite different, and even if any slight resonance did occur, it would not favour either of the substances used. (There is, moreover, no necessity for taking observations on both pendulums simultaneously. It is sufficient, if a good clock be used, to take them alternately.) To set the pendulums in motion, tubes with rubber bulbs are used, by means of which puffs of air can be projected against the bobs.

In taking observations a flashing apparatus is employed. It consists of a clock capable of giving electrical signals each second, a lever actuated by these and arranged so as to interrupt the primary current of an induction coil, the said coil, and a helium tube, which is connected to the secondary of the coil. For most of this apparatus, the writer is indebted to Dr. F. Horton, who has described it in detail.* The helium tube is set up horizontally on a shelf fixed to the wall of the room opposite the pendulums, at a distance from them of 4.8 metres and about 0.3 metre above the level of the mirrors. A cylindrical concave mirror is placed slightly behind and below the tube, so as to give a fine and sharp line-image each time a flash occurs. This image is observed by reflection in the pendulum mirrors by means of telescopes, one

* See 'Phil. Trans.,' A, vol. 204.

for each pendulum. These telescopes stand on a shelf fixed to the wall about 1 metre in front of the mirrors. The telescopes tilt slightly upward towards the mirrors, and the rays from the flashing apparatus to the mirrors pass just above the observer's head. As the clock which controls the flashes is in another part of the laboratory, a chronometer is placed near the telescopes for the indication of time.

4. *Method of Experiment.*

It is necessary, as has been explained in section 2, to make determinations of the times of swing of the experimental pendulum about its two knife-edges for various positions of the bob, one of the substances to be experimented upon being contained therein, and then to change to the second substance and repeat the series of observations. As, however, only comparative determinations are required, it is not necessary to express the times in seconds. Any other invariable unit of time will do equally well. The unit actually adopted is nearly 1 second, it is $T/1.9601$, where T is the time of a complete swing of the standard pendulum under normal conditions of temperature, air density, and amplitude of oscillation, and 1.9601 is approximately the average value of the time of the standard as determined directly in the experiment in clock seconds. T is assumed to be accurately constant during a series of observations. Its absolute value is not required, and has not been determined by reference to transit observations—it is, of course, very nearly 1.9601. Corrections are made for changes from the normal density of the air, but corrections for variation of amplitude and temperature of the pendulum itself (the rod of which is of invar) are negligibly small and have not been applied.

Now suppose the time of the experimental pendulum, and also that of the standard, to be observed in clock seconds, then if their actual times are t and T in mean solar seconds, and if the clock second is equal to c mean solar seconds, the observed times will be t/c and T/c respectively, so that we shall have, as the ratio of the observed time of the experimental pendulum to that of the standard, $t_c/T_c = t/T$, which is the actual time of the experimental pendulum in terms of that of the standard. In order to express this in units more nearly equal to 1 second, t/T may be multiplied by 1.9601, which will give the actual time of the experimental pendulum in terms of $T/1.9601$, the unit described above. The finally tabulated times of the experimental pendulum will be given by—

$$\text{Tabulated time} = \frac{\text{obs. time of exp. cor. for temp., etc.} \times 1.9601}{\text{obs. time of st. cor. for dens. of air}}.$$

The observations are made by a method of coincidences due to Prof. Poynting, and described by Dr. Horton in the paper referred to above. One or two modifications in the procedure have however been made in the present case. The method as used will be understood from the following description. Suppose the pendulum which is to be timed and the flashing apparatus to be working, we shall observe, on looking through the telescope, whenever a flash occurs, two images of it in the field of view. One of these, due to the fixed mirror, will have a constant position in the field, the other, due to the mirror attached to the pendulum, will in general be seen in a new position each second. The fixed mirror should be adjusted so that when the pendulum is vertical, the two images are seen to be in the same straight line and partially overlapping. Now suppose that at some instant a perfect coincidence of the images occurs. If there is no special relation between the period of the pendulum and that of the flashes, the moving image will then appear to dart about the field in an erratic manner. After a time it will occupy a position near to the fixed image, but probably not exactly coinciding with it. Let this occur n seconds after the first coincidence. At this instant the pendulum will be nearly vertical, and if it is moving in the same direction as when the first coincidence occurred it will have executed almost, but not quite, exactly a whole number, say N , of swings. Suppose it to have passed a little beyond its central position, so that the actual number of swings is $N + \alpha$, where α is a small fraction. In this case the pendulum may be said to be gaining on the flashes. In n seconds then the pendulum will have executed $N + \alpha$ swings.

Again, in another n seconds the moving image will appear a little further from the zero (or fixed image), and so on. After a time the image will reach its maximum distance from the zero, and at that instant the pendulum will be at one extremity of its swing, and it will have gained one-quarter of a complete period on the flashes. The image will then begin to return towards the zero. When it reaches it, the pendulum will have gained half a complete swing. The image will then pass along to the other extremity of its range, and again return to the zero. We will suppose that an exact coincidence then occurs. At that instant the pendulum will have gained exactly one complete swing on the flashes, and the observation will terminate. All the flashes except those occurring at intervals of n seconds will, of course, have been ignored. Let the total number of periods of n seconds each be P , then we know that the pendulum will have executed $PN + 1$ swings in Pn seconds, and its time of swing is thus $Pn/(PN + 1)$.

In general, however, exact coincidences do not occur, and it is necessary to observe two successive positions of the image, one on each side of the zero,

and to estimate their distances from it. Let the early image occur at a distance a in front of the zero, and the late one b behind it. Then, if we count the periods from the first flash, their total number must be diminished by $a/(a+b)$ of a period, for this fraction of a period elapsed before the ideal coincidence took place. Similarly, a correction must be made at the end of the observation, should a perfect coincidence not occur. In order to enable these distances to be estimated, scales, slightly illuminated, are used in the eye-pieces of the telescopes.

There are two sources of error in practice which need attention. In the first place, an error may arise due to an irregularity of the flashes caused in the following way. The clock pendulum is fitted with a platinum projection, which cuts through a fine stream of mercury and so makes contact each time it passes its mid-position. Now, should the projection or the mercury stream be slightly displaced laterally, so that contact always occurs when the pendulum is a little to one side of its mid-position, it is evident that the contacts will take place at unequal intervals. Alternate contacts will, however, take place at two-second intervals. Thus in the actual observations n must always be an even number; this ensures freedom from error due to the above cause. Again, the images in the field of view may not exactly coincide when the pendulum under observation is in its central position, and in this case the true zero is not accurately indicated by the fixed image. This would be of little importance if the amplitude of the pendulum remained constant. But, as this is not the case, an error is introduced if we take the fixed image as representing the zero. This error is practically eliminated by taking two independent (but overlapping) observations of the time, one being started with a coincidence which occurs while the pendulum is moving towards the observer, and the other with one which occurs when the pendulum is in opposite phase. The mean of these times is to be taken as the observed time. The actual procedure is as follows:—First, the experimental pendulum is set on its lower knife-edge and set into motion; the standard is also started. After 10 or 15 minutes the two observations on the experimental pendulum are commenced, and then the two on the standard. In due course the experimental observations are completed, the pendulum stopped, and set on its upper knife-edge and restarted. After a few minutes two observations on it are commenced; these are completed, and finally the two standard observations are completed. The value of P for each of the six observations is then recorded. Records are also kept of initial and final amplitudes, of the readings of the thermometers and of the barometer, and of a maximum and minimum thermometer (in the mornings only) kept in the case to show the range of temperature during the previous 24 hours.

The filling of the bob is an important operation. As has been shown, slight variations in the position of the centre of gravity are in themselves unimportant, but errors are introduced by changes in the moment of inertia of the bob about an axis through its centre of gravity. With reasonable care these can be rendered negligibly small. The substances used are red lead and uranium oxide. To the latter, however, it has been found necessary to add a small proportion of magnesium oxide, to render it similar to the red lead in packing properties. The method of packing finally adopted is as follows:—The substance is divided into three equal portions by weight, and one of these is put into the bob. The bob is then tapped underneath, to cause the substance to nearly settle down into the lower third of the bob. Then a flat disc of brass is lowered on to the substance, and on this is placed a distance piece, which is pressed down until its top is exactly level with the rim of the bob. By this means the substance is slightly compressed into a definite volume into the lower part of the bob. The disc, etc., are then removed and the second portion of the substance is put into the bob, and a similar process gone through, using a shorter distance piece. Finally, the remainder of the substance is put in and tapped down as before, and pressed home by means of the lid of the bob, which is then secured by its nut, care being taken to always screw down this nut to the same extent. Greater accuracy of packing could be attained by multiplying the stages of the process, but the three stages have been found to be sufficient for the purposes of this experiment.

As regards the amplitudes of oscillation, these were practically identical in the several experiments. The initial and final amplitudes were—

Standard pendulum	0° 11'—0° 7'
Exp. pendulum, upper K.E.	0° 10'—0° 7'
„ lower K.E.	0° 10'—0° 5'

5. *Experimental Results.*

In Table I some constants of the pendulum are given. They have been carefully determined,* though strict accuracy is not essential in the case of quantities which remain constant throughout the whole series of experiments.

Table II summarises the records of observations of the final experiments. Two experiments were usually made in a day, one in the morning and one in the afternoon. The substance was usually changed once a day after the morning observation. In the table, the mean values for P (see p. 335)

* The position of the c.g. of the bob and substance has been assumed in determining these constants. In the experiments this c.g. varies, and in this respect the numbers in the table are not actually constants.

Table I.

	Mass.	Distance of c.g. from upper K.E.	Ma about upper K.E.	Ma about lower K.E.	I about its own c.g.	I about upper K.E.	I about lower K.E.
Rod with fixtures (except knife-edges)	grammes.	cms.					
Upper K.E.	1401.983	+ 67.040	+ 93.998.5	—	—	8,613,594.8	2,400,618.7
Lower K.E.	29.285	— 0.427	— 12.5	—	—	15.0	166,434.3
Adjustable weight	29.083	+ 74.528	+ 2,167.5	—	—	161,551.8	14.4
Bob (empty)	179.770	+ 12.947	+ 2,327.5	—	—	30,433.2	691,580.2
Substance	267.410	+ 139.945	+ 37,423.8	—	—	5,242,217.8	1,133,901.9
	1035.816	+ 139.988	+ 144,981.3	—	—	20,300,142.9	4,385,070.9
<i>Summary.</i>							
Rod, etc.	1640.121	+ 60.039	+ 98,471.0	—	2,893,480	8,805,594.8	—
Bob and substance	1808.228	+ 139.963	+ 182,404.1	—	12,640	25,542,360.7	—
Total pendulum	2943.347	+ 95.427	+ 280,875.1	+ 60,247.36	7,544,916	34,347,955.5	8,777,620.4

Table II.

No. of experi- ment.	Date.	P.		Temperature.		Pressure.	Range of temperature in last 24 hours.	Position of bob.	Substance used.
		Standard pendulum.	Experimental pendulum.	Air.	Metal.				
	April, 1910.			° C.	° C.	mm. Hg.	° F.		
1	Wed., 13th, morn....	57.07	73.48	83.83	11.7	11.40	740.40	1.5	Lead.
2	" " aft.	57.42	68.91	81.18	12.0	11.75	739.13	—	Uranium.
3	Thurs., 14th, morn....	56.52	73.31	83.34	12.0	11.85	742.68	1.0	Lead.
4	" " aft.	56.71	67.45	80.60	12.2	12.00	741.92	—	"
5	Fri., 15th, morn....	56.93	68.21	81.96	12.1	11.85	743.44	1.5	Uranium.
6	" " morn....	56.66	73.63	83.50	11.85	11.65	762.24	1.0	Lead.
7	Tues., 19th, morn....	57.16	70.88	82.06	12.25	11.95	762.49	—	Uranium.
8	" " aft.	55.99	70.93	83.27	12.25	12.05	767.83	0.5	Lead.
9	Wed., 20th, morn....	56.08	71.97	82.61	12.5	12.25	766.05	—	"
10	" " aft.	55.14	72.65	83.19	12.7	12.55	763.76	1.0	Uranium.
11	Thurs., 21st, morn....	55.58	73.65	83.19	12.7	12.55	763.76	—	Lead.
12	" " aft.	55.78	71.70	82.48	12.95	12.80	764.02	—	"
	Fri., 22nd, morn....		72.89	82.89	12.9	12.75	761.22	1.0	"

are given for the standard and for the upper and lower knife-edge observations on the experimental pendulum. The values of N and n , and the number of swings gained or lost during the observations, are as follows:—

Standard pendulum.....	$N = 51, n = 100,$	gains 1 swing.
Exp. pendulum, upper K.E.....	$N = 9, n = 20,$	gains 1 swing.
„ lower K.E.....	$N = 14, n = 34,$	loses 2 swings.

The position of the bob is given in each case, N indicates normal position, and L a position somewhat lower than the normal and different in the different cases. The other columns of the table require no special explanation.

The observed times, as obtained from the values of P by the method which has previously been explained, are given in Table III. Three sets of corrections are also given in the table. As has been shown, it is only necessary to correct for variations from the normal conditions under which the experiments are made. The normal temperature is taken to be 12°C . and the pressure 76 cms. In the first place, corrections are given for deviations in the temperature of the experimental pendulum from 12° . These are obtained in a manner which has been described in section 2.

The coefficient of expansion is taken to be 0.000019. Taking approximate values of t for upper and lower knife-edges, we have

$$\frac{1}{2}at \text{ for upper knife-edge} = 0.000021 \text{ sec.}$$

$$\frac{1}{2}at \text{ for lower „ „} = 0.000023 \text{ „}$$

Thus for a rise of 1°C . we reduce the times by the above quantities.

Corrections are next given for variations in the pressure. In order to obtain these it is necessary to know the increments of the values of I and Mh in the expression for the time of swing of the pendulum under consideration. Thus, for example, in the case of the experimental pendulum swinging about its upper knife-edge, we have

$$t^2 = \frac{4\pi^2}{g} \frac{I}{Mh} = Q \frac{I}{Mh}, \text{ say.}$$

From Table I we see that $t^2 = Q 34,347,955/280,875.1$.

Now, from a knowledge of the dimensions of the apparatus, it is easy to calculate with sufficient accuracy the changes produced in I and Mh by an increase of pressure of 1 cm. of mercury. In making this calculation, regard must be paid to the points mentioned on p. 330. In the above case, an increase of pressure of 1 cm. gives rise to an increase of I of 167, and a decrease of Mh of 0.7. Thus the new time will be given by $t_1^2 = Q 34,348,122/280,874.4$, so that we have $t_1 = 1.0000038t$,

Table III.

No. of experiment.	Observed times.			Corrections for temperature of experimental pendulum.			Corrections for atmospheric pressure.			Corrections for atmospheric temperature.		
	Standard pendulum.	Experimental pendulum.		Upper K.E.	Lower K.E.	Standard pendulum.	Experimental pendulum.		Standard pendulum.	Experimental pendulum.		Lower K.E.
		Upper K.E.	Lower K.E.				Upper K.E.	Lower K.E.		Upper K.E.	Lower K.E.	
1	1-960111	2-218867	2-432717	+	+0-000013	+	+0-000014	+0-000008	+0-000017	+0-000024	-0-000001	-0-000001
2	115	644	852	+	005	+	006	+	018	025	000	000
3	104	813	741	+	003	+	003	+	015	021	000	000
4	107	563	884	+	000	+	000	+	015	022	000	001
5	109	660	812	+	003	+	003	+	014	020	000	000
6	106	874	733	+	007	+	008	001	002	003	000	000
7	112	744	807	+	001	+	001	001	002	003	000	001
8	098	746	796	-	001	-	001	003	006	009	001	001
9	099	796	778	-	005	-	006	002	005	007	001	002
10	087	829	748	-	012	-	013	001	003	004	001	002
11	093	783	795	-	017	-	018	002	003	005	002	003
12	095	840	764	-	016	-	017	000	001	001	002	003

which is found to mean that the increase of pressure causes an increase of t represented by $8\frac{1}{2}$ units in the last place of decimals tabulated. Therefore, to reduce the observed times to times for normal pressure, it is necessary to deduct $8\frac{1}{2}$ units from the last decimal place for each centimetre of pressure greater than 76. In the case of the lower knife-edge 12 units are to be deducted, and in the case of the standard, 4 units. The effect of a fall of 1° C. in the temperature of the air is to that of an increase of pressure of 1 cm. as 76 : 285. The corrections given in the table for changes of atmospheric temperature are based on this fact.

Table IV.

No. of experiment.	Corrected times.			Tabulated times.	
	Standard pendulum. (a)	Experimental pendulum.		Upper K.E. $\left(\frac{b}{a} \times 1.9601\right)$.	Lower K.E. $\left(\frac{c}{a} \times 1.9601\right)$.
		Upper K.E. (b)	Lower K.E. (c)		
1	1.960119	2.218896	2.432754	2.218874	2.432781
2	123	667	883	641	854
3	111	831	765	819	751
4	114	583	907	567	889
5	116	677	835	659	816
6	105	879	738	873	732
7	111	744	806	731	792
8	095	740	787	745	793
9	097	787	767	790	770
10	087	815	733	829	748
11	092	765	765	774	774
12	096	825	749	829	754

The corrected times are given in Table IV, together with the "tabulated times." In these, as was explained on p. 334, the clock errors are eliminated, and the times of the experimental pendulum are expressed in invariable units closely approximating to seconds.

The tabulated times can now be plotted, and the characteristic lines obtained for the two substances. We may first, however, determine the amount by which they will be separated on the supposition that the theory given at the beginning of the paper holds true. We first require the approximate mass of radium equivalent in the radioactive substance used. The mass of uranium oxide is 1015 grammes, and assuming the composition to be given by U_2O_5 , we shall have 860 grammes of uranium, corresponding to 811 grammes of radium. The extra mass attached to each gramme of radium is $1/13$ th milligramme. This gives 62 milligrammes for 806 grammes

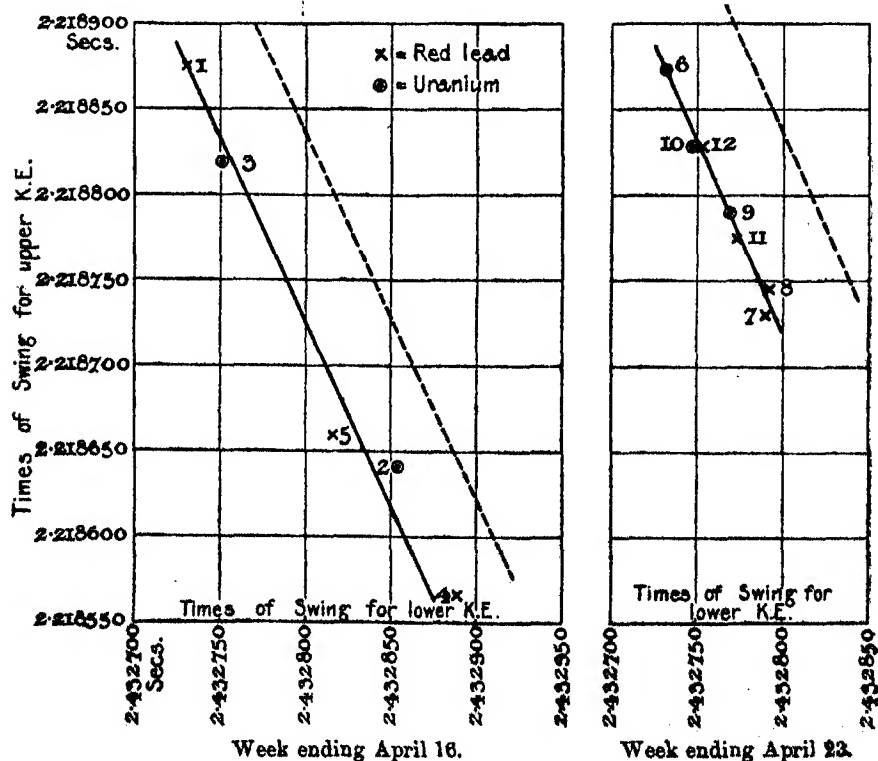
of radium. This will allow for the presence of a little foreign matter in the substance used. It is necessary, then, to determine the variation in the time of swing produced by the addition to the bob of a mass of 0.062 gramme, no change being made in the weight of the bob. The effect of the increase of mass is merely to increase I about the upper knife-edge by 1215, and I about the lower knife-edge by 262.

Now
$$t^2 = \frac{4\pi^2 I}{Wh} \text{ so that } \frac{2dt}{t} = \frac{dI}{I}.$$

From the upper knife-edge $dt = \frac{2.2187}{2 \times 34,347,955} \times 1215 = 0.000036 \text{ sec.}$

From the lower knife-edge $dt = \frac{2.4328}{2 \times 8,777,620} \times 262 = 0.000036 \text{ sec.}$

These increments of time represent the vertical and horizontal separations of the characteristic lines of the non-radioactive and the radioactive substances, according to the theory. The effect is indicated on the diagrams which follow :—



6. *Conclusion.*

It is evident from the diagrams that the characteristic lines for the two substances are identical within the limits of experimental error. In the experiments exhibited on the first diagram, the accurate method of packing was not in use, and the weather conditions were not quite so favourable as they were during the week following. In the second diagram, the advantage of the better system of packing, and also of the more uniform weather which prevailed, are well shown. The dotted lines are drawn parallel to the experimental characteristic lines, so as to show the distance which should separate the lead and uranium lines, according to the theory. In the more accurate diagram, the deviations from the line are not greater than 1 in 600,000 on the times. The results indicate that the ratio of mass to weight for uranium oxide does not differ from that for lead oxide by more than 1 part in 200,000.

It remains to show that inaccuracies in the weighing of the bob are not likely to cause appreciable errors. Following the method of p. 339, we have for the normal time from the upper knife-edge $t^2 = Q\ 34,347,955/280,875.1$. Now, suppose we add 0.01 gramme to the bob, the increase in I (the numerator) will be about 196, and the increase in Mh (the denominator) about 1.4. Thus, for the new time, we have $t_1^2 = Q\ 34,348,151/280,876.5$, which gives $t_1^2 = 1.000001t^2$ or $t_1 = 1.0000005t$, which is an increase of 1 in 2,000,000, and is therefore negligible, which is also the case if the lower knife-edge be considered, though the effect is somewhat greater, viz., about 1 in 300,000. It is, of course, easy to reduce the errors to smaller dimensions than these by careful weighing.

An effect which caused considerable trouble during the experiments may be briefly referred to. A rod of nickel steel was first used on account of its small coefficient of expansion. Sometimes for two or three days satisfactory results would be obtained, then the characteristic line would suddenly take up a new position to the left of the old one. This took place time after time, the line always moving parallel to itself in the same direction. A rod of tool steel exhibited the same error. It appeared to be due to magnetic effects. The rods became magnetised by induction in the earth's field, and no doubt this magnetisation was assisted by the movements of the pendulum when it was transferred from one knife-edge to the other, and during the removal and readjustment of the bob. The cast-iron bracket was probably concerned in the matter. The rod of the standard pendulum was also magnetic, but it remained untouched during the whole course of the experiments, and gave rise to no difficulty. It had, at any rate, settled down to a

very steady state by the time the final experiments were made. In all cases some irregularity took place when new knife-edges were used, due no doubt to the wearing off of some slight "burr" left on the edge during sharpening.

The pendulum was sensitive to sudden variations of the weather. It would be a great advantage to enclose the apparatus in a case kept at constant temperature and pressure. A somewhat improved method of removing and replacing the bob is also desirable.

In conclusion, the writer wishes to express his best thanks to Prof. Sir J. J. Thomson for his unfailing kindness throughout the course of this investigation.

On the Spontaneous Crystallisation and the Melting and Freezing Point Curves of Mixtures of Two Substances which form Mixed Crystals and possess a Minimum or Eutectic Freezing Point.—Mixtures of Azobenzene and Benzylaniline.

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The behaviour of mixtures of naphthalene and β -naphthol has already been investigated, and the freezing and melting point curves and the curve of

spontaneous crystallisation for these mixtures described.* These substances were found to form a continuous series of mixed crystals, on a curve of Roozeboom's Type 1, the melting and freezing points of all the mixtures lying between the melting points of the pure substances.

The behaviour of mixtures of monochloroacetic acid and naphthalene was also investigated,† for it was stated by Cady‡ that these substances form mixed crystals of Roozeboom's Type 5, whose melting and freezing point curves exhibit a minimum or eutectic freezing point. Experiments were therefore made with these substances with the object of determining the form of the curve of spontaneous crystallisation, or supersolubility curve, for mixtures of this type. No sign of the formation of any mixed crystals was observed, however, in a lengthy series of experiments, and it was shown that naphthalene and monochloroacetic acid give the ordinary V-shaped freezing point curve for the solutions of two substances in each other, similar to that already obtained for mixtures of salol and betol,§ the only new feature being introduced by the existence of three modifications of monochloroacetic acid. The monochloroacetic acid and naphthalene mixtures having thus failed as an example of mixed crystals possessing a minimum or eutectic freezing point, another attempt was made to obtain a pair of substances with convenient melting points which form mixed crystals and possess the melting and freezing point curves with minimum eutectic point characteristic of Roozeboom's Type 5.

Azobenzene and benzylaniline were chosen for this purpose, and the present paper deals with mixtures of these substances.

CRYSTALLINE FORM OF BENZYLANILINE AND AZOBENZENE.

Benzylaniline, $C_6H_5CH_2NH\ C_6H_5$, has been described by Jaeger,|| who obtained transparent colourless crystals from a solution in methyl alcohol.

He found the crystals to be monoclinic, with axial ratios—

$$a : b : c = 2.1076 : 1 : 1.0948,$$

and

$$\beta = 76^\circ 36\frac{1}{2}'.$$

The habit is elongated along the b -axis, the plane of the optic axes being (010). The axial dispersion is strong, with $\rho > v$.

Azobenzene, $C_6H_5NNC_6H_5$, has been described by Boeris,¶ and by Calderon.**

* 'Journ. Chem. Soc.,' 1908, vol. 93, 1, p. 927.

† 'Phil. Trans.,' 1909, A, vol. 209, p. 337.

‡ 'Journ. Phys. Chem.,' 1899, vol. 3, p. 127.

§ 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 322.

|| 'Zts. für Kryst.,' 1907, vol. 42, p. 265.

¶ 'Zts. für Kryst.,' 1901, vol. 34, p. 301.

** 'Zts. für Kryst.,' 1880, vol. 4, p. 234.

The former obtained tabular orange-coloured crystals of azobenzene, from a solution in acetic ether, which he describes as monoclinic, with axial ratios—

$$a : b : c = 2.1076 : 1 : 1.3312,$$

and

$$\beta = 65^\circ 34'.$$

The plane of the optic axes is perpendicular to (010), and nearly parallel to (001), and there is considerable axial dispersion, $\rho < v$. Jaeger* points out that, although it is possible by a suitable choice of parametral faces to obtain similar axial ratios for the crystals of benzylaniline and azobenzene,

$$(\text{Azobenzene} \dots \dots a : b : c = 2.1076 : 1 : 1.4220, \beta = 76^\circ 32')$$

$$\text{Benzylaniline} \dots a : b : c = 2.1076 : 1 : 1.6422, \beta = 76^\circ 36'),$$

yet this would require an unnatural position for the crystals, involving high indices for some of the forms observed, so that the relation between the two substances is a somewhat distant one.

Jaeger† gives the melting points of pure azobenzene and benzylaniline as 68° and 36.5° . He also gives the melting points of a few mixtures of these substances, which he states form mixed crystals and show a minimum eutectic point. He obtained mixed crystals of azobenzene and benzylaniline from solution in alcohol and chloroform as small red needles, which were strongly pleochroic, but unsuitable for crystallographic investigation.

Calderon‡ gives the melting point of azobenzene as 66.5° , while Pickering§ gives 66.8° .

Mixtures of azobenzene and benzylaniline have also been investigated by Bruni and Gorni,|| and by Garelli and Calzolari;¶ these authors do not, however, give any melting points for actual mixtures, but state that azobenzene and benzylaniline form mixed crystals, and exhibit abnormal cryoscopic behaviour.

MICROSCOPIC EXAMINATION OF AZOBENZENE AND BENZYLANILINE CRYSTALLISED FROM FUSION.

In the present investigation azobenzene and benzylaniline were first examined under the microscope as a thin film crystallised from fusion on a microscope slide under a cover glass.

* *Loc. cit.*

† 'Zts. für Kryst.,' 1907, vol. 42, p. 265.

‡ 'Zts. für Kryst.,' 1880, vol. 4, p. 234.

§ 'Phil. Mag.,' (5), 1895, vol. 39, p. 510.

|| 'Real. Accad. dei Lincei,' 1899, vol. 8, pp. 454 and 470.

¶ 'Real. Accad. dei Lincei,' 1899, vol. 8, p. 579, and 'Gazetta,' vol. 29, ii, p. 259.

Azobenzene appears as stout radiating prisms and irregular plates of a fine orange colour. The plates and most of the prisms are strongly pleochroic, the colours being orange and yellow. The extinction of the prisms is usually straight or nearly so, but on some it is oblique with angles ranging to about 35° . Many of the prisms do not become dark at all, but show a strong red and green coloration about the position of extinction, owing to strong dispersion of the optic axes. With convergent light, some of the prisms with straight extinction show an interference figure resembling that of brookite, with a positive acute bisectrix in the centre of the field. The optic axial plane is parallel to the length of the prisms, and the dispersion $\rho < v$, the crystals being nearly uniaxial for red light. The plates commonly show, in sodium light, hyperbolic bands indicating the slightly oblique emergence of an obtuse bisectrix or third mean line.

These appearances agree with the description of the crystals given by Boeris,* the prismatic outlines being due to a vertical or oblique position of the thin tabular crystals.

Benzylaniline, examined in the same way, showed stout colourless blades growing radially from centres, with approximately straight extinction. In convergent light the needles show a wide angle negative bisectrix, nearly central, the axial plane being perpendicular to the length of the needles. In some of the needles a single optic axis is visible at the edge of the field.

The plates and needles of azobenzene and benzyaniline obtained from fusion on the microscope slide rarely possess angles measurable under the microscope, their edges being rounded or ragged.

Crystals formed in drops of azobenzene dissolved in benzene or alcohol were also examined under the microscope. They were rhombs with an angle of 49° and diagonal extinction. Viewed in convergent light these rhombs showed an obtuse bisectrix or third mean line.

Drops of benzyaniline dissolved in toluene or ether gave needles with angle of 72° approximately, the extinction being always parallel to the length of the needles. Viewed in convergent light these needles showed a normally emergent bisectrix, both optic axes being visible.

MIXTURES OF AZOBENZENE AND BENZYLANILINE.

Mixtures of azobenzene and benzyaniline were next investigated, and the freezing and melting point curves for these mixtures were determined.

* *Loc. cit.*

The Freezing Point Curve.

To obtain the freezing point curve the mixtures varying in concentration from 100 per cent. azobenzene to 100 per cent. benzyaniline were enclosed in sealed glass tubes. Each mixture was heated in a water bath until it was completely melted, with the exception of one or two small crystals at one end of the tube. These crystals were watched with a lens as the temperature of the bath was lowered, until a temperature was reached at which equilibrium was found to exist between them and the liquid mixture. This temperature, at which the crystals neither grew nor dissolved, was taken as the freezing point of the mixture. This method has been fully described.*

The results obtained appear tabulated below :—

Percentage composition of mixture.		Freezing point.	Percentage composition of mixture.		Freezing point.
Azobenzene.	Benzyaniline.		Azobenzene.	Benzyaniline.	
100	0	66	19·972	80·028	27
90·025	9·975	62·5	19·122	80·878	26·5
88·61	11·39	61·5	17·958	82·042	27
80·076	19·924	58	15·579	84·421	29
70	30	53·5	15	85	28·5
59·81	40·19	48	10·437	89·563	31
50	50	42·6	5·187	94·813	33
40	60	35	5·018	94·982	33
34·8	65·2	33	2·506	97·494	34·5
29·868	70·132	30·5	0	100	35·5
20·054	79·946	27			

These freezing points, when plotted on the concentration-temperature diagram, give the ordinary V-shaped freezing point curve, with a minimum or eutectic point at 26·5° for the mixture 81 per cent. benzyaniline, 19 per cent. azobenzene.

On the side which shows excess of benzyaniline this curve is almost a straight line, but on the side showing excess of azobenzene the curve is slightly concave towards the concentration axis.

The Melting Point Curve.

To obtain the melting point curve the same tubes were used as in the experiments on the freezing point curve. The tubes containing the various mixtures were heated in turn and shaken until the crystals had completely melted. Each tube was then cooled, and the liquid mixture allowed to

* 'Journ. Chem. Soc.,' 1908, vol. 93, 1, p. 931.

solidify completely. As with all substances forming mixed crystals, the solid first deposited differs in composition from the original liquid, and as the temperature continues to fall, different mixed crystals form, whose composition approximates more and more nearly to that of the original liquid, until the very last mixed crystals that form should have the exact composition of the original liquid taken. Crystals of this composition, therefore, have a lower melting point than any of those previously deposited.

When the mixture was completely solid the tube was immersed in a cold water bath, the temperature of which was raised very slowly while the solid mixture was watched carefully with a lens. At first the mixture is quite compact and solid, but when the temperature has been raised to a certain point some of the crystals are seen to begin to melt; parts of the mixture appear slightly sticky; and, on further raising the temperature very slightly, if the tube be inverted a little liquid stream starts running down the sides. This point is taken as the melting point of a mixture whose composition is the same as that of the original liquid taken. The melting point curve thus obtained agrees very approximately with some later experiments described on pp. 352-4, in which the melting point curve was obtained directly by analysis of the mixed crystals.

Each experiment was repeated several times, and the temperature at which melting was first observed was very carefully noted. All the melting points are thus determined with rising temperature, the following being the tabulated results:—

Percentage composition of mixture.		Melting point.	Percentage composition of mixture.		Melting point.
Azobenzene.	Benzylaniline.		Azobenzene.	Benzylaniline.	
100	0	66	19·972	80·028	26
90·025	9·975	54	19·122	80·878	26
80·076	19·924	46	17·958	82·042	26
70	30	42	15·579	84·421	26
59·81	40·19	37	15	85	26
50	50	32·4	10·487	89·513	26
49·92	50·08	32·5	5·187	94·813	26
40	60	29	5·018	94·982	26
34·8	65·2	26	2·506	97·494	26
29·868	70·132	26	0	100	35·5
20·054	79·946	26			

When plotted on the concentration-temperature diagram these points give the complete melting point curve for all mixtures of azobenzene and benzylaniline. As will be seen from the diagram, part of the melting

point curve is flat, and runs parallel to the concentration-axis, and mixtures of all concentrations between 35 per cent. azobenzene 65 per cent. benzyraniline, and 2.5 per cent. azobenzene 97.5 per cent. benzyraniline, start melting at the same temperature, viz., 26° . Hence, no mixed crystals are deposited on the side of the eutectic weak in azobenzene, but only pure benzyraniline, which grows as soon as the temperature given by the freezing point curve is reached, until the mixture reaches the eutectic composition, when the rest of the liquid solidifies as a mixture of pure benzyraniline with the mixed crystals containing 35 per cent. azobenzene and 65 per cent. benzyraniline, whose melting point is 26° . This result is confirmed by the microscopic examination of the solidified mixtures as described below (p. 354). On the other side of the eutectic, however, in mixtures containing excess of azobenzene, a series of mixed crystals are formed which contain from 100 per cent. to 35 per cent. of azobenzene. As has been shown above (p. 348) a mixture of approximately 81 per cent. benzyraniline 19 per cent. azobenzene freezes at 26.5° , where the curve exhibits a eutectic point. A mixture of this composition, therefore, melts and freezes very approximately at the same temperature. This is the invariant point, and on either side of it different solids exist in equilibrium with the liquid. At this point four phases can co-exist, namely, mixed crystals containing 35 per cent. of azobenzene, pure benzyraniline, liquid solution, and vapour.

The melting point curve was not at first obtained in the form here described. In the first experiments, the flat part of the curve which extends from 65 to 100 per cent. of benzyraniline, appeared only to extend from 65 to 85 per cent. of benzyraniline. Mixtures containing between 85 and 97.5 per cent. benzyraniline, which were allowed to solidify spontaneously in a sealed tube and were then reheated, appeared to start melting at temperatures varying from 27° to 33° , instead of at 26° , as subsequently found. As originally plotted, therefore, the melting point curve pointed to the existence of two series of mixed crystals, one on each side of the eutectic. Further careful experiments showed, however, that mixed crystals do not really separate on the side of the eutectic containing excess of benzyraniline, but pure benzyraniline only.

Experiments made under the microscope by examining the crystals growing from drops of these mixtures on a slide, showed that the first crystals separating from mixtures containing more than 81 per cent. of benzyraniline are pure white in colour, and show no trace of the orange colour of the azobenzene, and are therefore probably pure benzyraniline. But, if pure benzyraniline only is first deposited from these mixtures until the eutectic composition is reached, the remaining liquid will solidify as a mixture of

pure benzylaniline with mixed crystals of composition 35 per cent. azobenzene 65 per cent. benzylaniline. All these mixtures, therefore, since they contain some proportion of mixed crystals of this composition, should start melting at 26° . As has been stated, this melting point was not at first noticed; but, in some later experiments, it was found that if the tubes containing the mixtures with 2.5, 5, and 10 per cent. of azobenzene were melted so as to leave a few small crystals in the tube, and then allowed to solidify slowly at not too low a temperature, on heating these tubes again a slight melting does occur at 26° . On the other hand, if these same tubes are heated until the mixtures are completely liquid, and are then cooled and shaken till they crystallise spontaneously at a low temperature, no melting can be detected at 26° , but only at from 27° to 33° .

This discrepancy may, perhaps, be due to the fact that in the latter case the mixtures have crystallised spontaneously in the tubes at temperatures considerably lower than their freezing points. The pure benzylaniline may have formed so suddenly and rapidly that the eutectic composition is overshoot, so much benzylaniline coming out of solution that the remaining liquid contains a higher percentage of azobenzene than the eutectic, and consequently forms mixed crystals containing more than 35 per cent. azobenzene, which have higher melting points than 26° . When, however, the same mixtures are allowed to solidify slowly after inoculation with benzylaniline, as stated above, the true melting point 26° is obtained. In connection with this point it may here be mentioned that it was found possible later on, in some experiments described below, to separate the very first crystals which formed spontaneously in the mixtures of azobenzene and benzylaniline containing small percentages of azobenzene. If pure benzylaniline is first deposited from these mixtures, the melting point of the crystals which first form should be 35.5° , the melting point of the pure benzylaniline. It was found that the crystals thus separated from all mixtures on the benzylaniline side of the eutectic, after being washed with benzene to get rid of the mother liquor, all melt at 35.5° . Thus the first crystals forming spontaneously from all these mixtures have the melting point of pure benzylaniline, and consequently no mixed crystals are formed on this side of the eutectic, but crystals of pure benzylaniline only, in the usual manner of mixtures of two substances which yield the ordinary V-shaped melting point curve.

In the experiments made to determine the freezing point curve, the mixtures were enclosed in sealed glass tubes, and the temperature of equilibrium was obtained between the liquid and a few small crystals of unknown constitution. If no mixed crystals are formed on the side of the eutectic showing excess of benzylaniline, the freezing point curve on this

part of the diagram must be the equilibrium curve between the liquid mixture and pure benzylaniline. This was proved to be true by some further experiments, in which mixtures containing 5, 10, and 15 per cent. of azobenzene were placed in open test tubes, immersed in a water bath and inoculated with a minute crystal of benzylaniline.

The equilibrium points so obtained were found to agree with the freezing point curve obtained above.

The Melting Point Curve Obtained by Analysing the Mixed Crystals.

The method of experimenting described above for obtaining the melting point curve appears to be somewhat rough and unsatisfactory; in order, therefore, to check and confirm this curve, the melting points of mixed crystals of known composition were determined as follows:—

Mixtures of azobenzene and benzylaniline of various compositions were dissolved in benzene in a beaker, and the liquid was stirred regularly by means of a water motor while the benzene evaporated slowly. The liquid was inoculated with a minute mixed crystal, and as evaporation proceeded a crop of small crystals in equilibrium with the solution was slowly deposited and whirled about in the liquid. When a sufficient quantity of crystals had formed, the solution was filtered off by means of an air pump, and the crystals obtained dry on the filter in a small platinum cone. The crystals were then powdered in a mortar and placed in an exhausted desiccator for several hours to dry off the last traces of benzene. Since these crystals represent a small crop grown from, and in equilibrium with, a comparatively large volume of solution, they may be taken to be very approximately homogeneous. If this is so, when placed in a capillary tube they will melt at an approximately constant temperature, and this was found to be usually the case. When the temperature was not quite constant, but extended through a range of 1° or 2° , the mean was taken to represent the true melting point. The melting point for any crop being ascertained, the crystals were next analysed in order to find their composition. The analysis was carried out by extracting the benzylaniline from a known weight of the crystals with dilute hydrochloric acid, the azobenzene being left undissolved.

Three extractions in warm acid were found sufficient to dissolve all the benzylaniline, and the pure azobenzene left behind was dried and weighed. In this manner the composition of the original crystals was obtained.

These experiments were repeated with a considerable number of different solutions of azobenzene and benzylaniline in benzene, each solution giving a different set of homogeneous mixed crystals. From these experiments it

is possible, therefore, to plot the melting point curve for the azobenzene-benzylaniline mixtures, since the composition and melting point of each homogeneous crop of mixed crystals are known.

The following are the details of these experiments :—

Mean melting point of mixed crystals grown from solution in benzene.	Percentage composition found by analysis.		Mean melting point of mixed crystals grown from solution in benzene.	Percentage composition found by analysis.	
	Azobenzene.	Benzylaniline.		Azobenzene.	Benzylaniline.
60	93.893	6.107	37.75	57.57	42.43
59.6	94.23	5.77	37	55.4	44.6
58.9	93.33	6.67	35.5	58.95	43.05
48.1	83.32	16.68	33.5	54.64	45.36
40.8	66.07	33.93	30.25	46.5	53.5

These results, when plotted on the concentration-temperature diagram, should give the melting point curve for the azobenzene-benzylaniline mixtures, each set of crystals giving a point on the curve. These points are all shown on the diagram by \oplus . It will be seen that some of these points lie slightly above the melting point curve originally obtained, though, on the whole, the new experiments may be considered to confirm the original curve fairly well. The later experiments seem to show, however, that the melting point curve, as plotted from the original experiments, is slightly too low. This result might have been expected from a consideration of the method employed, for it was assumed that the last drop of the liquid to solidify gives crystals having the original constitution of the liquid. This would, no doubt, be the case if the cooling of the liquid were sufficiently slow, so that as the mixed crystals grew there was sufficient time for the equilibrium to be maintained by a continuous readjustment between the crystals and the liquid. But if the cooling is not sufficiently slow it is probable that the readjustment is incomplete, so that the last mixed crystals formed contain a slightly larger percentage of benzylaniline than the original mixture. These crystals would, therefore, have a slightly lower melting point than those having the composition of the original liquid. The later experiments, in which the mixtures were analysed, tend to show that this is the case, although the discrepancy is very slight, and does not appear to amount to more than approximately 1° of temperature.

The melting points for azobenzene and benzylaniline obtained above are 66° and 35.5° . On comparing these values with those previously obtained,

it will be seen that they are slightly lower than Jaeger's values 68° and 36.5° , and agree more nearly with those of Calderon and Pickering, who give the melting point of azobenzene as 66.5° and 66.8° respectively. The slightly lower values obtained in these experiments would seem to indicate that in all probability some small amount of impurity exists in the substances used in this research.

We may also compare the melting points obtained by Jaeger for the few mixtures of azobenzene and benzyaniline he examined with those obtained above. Jaeger's values are :—

Percentage composition of mixture.		Melting point:
Azobenzene.	Benzyaniline.	
6.5	93.5	35
12	88	32.5
51.4	48.6	49
76.8	23.7	61.5

It will be seen that these values for the melting points are considerably higher than those indicated by the diagram.

Microscopic Examination of Mixtures of Azobenzene and Benzyaniline Crystallised from Fusion.

A great number of drops of different mixtures were allowed to crystallise on the microscope slide at the temperature of the surrounding air, and the crystals were examined as they grew.

Various mixtures, containing 10, 20, 30, 35, 40, and 60 per cent. of azobenzene, were examined in this way.

The crystal needles first forming in the 10 per cent. mixture were colourless, and some colourless crystals also appeared in the 20 per cent. mixture. The remaining mixtures gave only coloured needles. The crystal needles were always formed with their oblique ends rounded or ragged, so that it was impossible to measure their angles, and when the liquid drop has completely solidified they form a confused mass intersecting each other in all directions. In all the mixtures the extinction was either straight or inclined at 1° or 2° to the length of the needles. Crystals grown from mixtures containing up to 30 per cent. azobenzene, when viewed in convergent light, usually showed both optic axes with the bisectrix nearly normal, although some of the needles showed only one optic axis on the edge of the field.

Needles grown from mixtures containing over 30 per cent. azobenzene always showed one optic axis only on the edge of the field. The axial plane always appears to be nearly perpendicular to the length of the crystal needles. That the colourless crystals which first appear in the mixtures weak in azobenzene are pure benzylaniline, is indicated by their optical properties.

The coloured crystals in the other mixtures are probably mixed crystals of various compositions. Some of these mixtures containing the larger proportions of azobenzene are very viscous, and remain partly liquid under a cover glass at the temperature of the room long after crystallisation has first started on the microscope slide.

Although these experiments were repeated several times, the results obtained do not appear to lead to very definite conclusions, the crystal needles being always ill-formed, with ragged edges. The temperature at which the needles grew on the slide was about 14° or 15° , so that it was considerably lower than the temperature at any point of the freezing point curve. The conditions of growth are therefore quite different, and at these lower temperatures the composition of the crystals separating from any liquid drop may differ from the composition of crystals separating from a similar drop at temperatures between the freezing and melting point curves determined above.

The Supersolubility Curve, or Curve of Spontaneous Crystallisation.

The freezing and melting point curves for mixtures of azobenzene and benzylaniline having been determined, an attempt was next made to plot the curve of spontaneous crystallisation for these mixtures, as has already been done for mixtures of naphthalene and β -naphthol.

Two methods of experimenting were employed, both of which have been used in the previous researches with Prof. Miers on spontaneous crystallisation, viz.: (1) the method of sealed tubes; (2) the measurement of the refractive indices of cooling mixtures.

(1) *Experiments with Sealed Tubes.*—Azobenzene, benzylaniline, and their mixtures were enclosed in sealed glass tubes which also contained some angular fragments of corundum to ensure friction.

The tubes containing the various mixtures were then heated in a water bath with frequent shaking until all the crystals had completely melted.

The water bath was then allowed to cool slowly, and as the temperature fell the tubes were shaken continuously, either by hand or on a rocking apparatus placed within the water bath. With each mixture it was found that when the temperature had fallen to a certain point, a dense shower of crystals suddenly appeared in the tube and the whole mixture rapidly

became solid. The temperature at which the shower occurs depends upon the composition of the mixture, and was found to be approximately constant for each mixture.

The experiment with each tube was, in general, repeated several times; the following table gives all the results obtained from 16 tubes treated in this manner:—

Percentage composition of mixture in tube.		Temperature of spontaneous crystallisation.
Azobenzene.	Benzylaniline.	
100	0	58°·5, 56°·5.
90·025	9·975	51°, 51°·5, 51°·5, 52°·2.
79·96	20·04	48°·5, 48°·5, 48°·5, 48°.
70	30	43°·5, 48°, 42°, 42°.
59·81	40·19	39°·6, 39°·5, 39°·5, 38°·5, 38°·5.
49·92	50·08	35°·5, 34°, 34°·7, 35°·2, 35°·5, 35°·5.
39·80	60·20	28°, 30°, 30°, 30°, 30°.
34·80	65·20	26°, 26°, 26°.
29·868	70·132	22°.
19·972	80·028	17°·5, 18°·5, 18°·4, 18°·4, 18°.
17·958	82·042	18°, 16°·2, 18°, 18°, 18°.
15·579	84·421	18°, 18°·1, 18°·2.
15	85	18°.
10·437	89·563	20°·5.
5·187	94·813	26°·5, 20°.
0	100	30°.

These results, when plotted on the concentration-temperature diagram, give the complete supersolubility curve, or curve of spontaneous crystallisation, for azobenzene, benzylaniline, and their mixtures. Where there was a slight variation in the temperature of spontaneous crystallisation of a single tube, the highest temperature obtained has been always taken as the true temperature of spontaneous crystallisation; in the other experiments the mixture must have passed slightly into the labile state, probably in consequence of too rapid cooling.

This curve, which is shown on the diagram, separates the metastable and labile areas for all mixtures of azobenzene and benzylaniline. Above this curve the mixed crystals cannot form spontaneously, although they will grow after inoculation, but below it mixed crystals can, and do, form spontaneously in a shower. As will be seen from the diagram the supersolubility curve runs roughly parallel to the freezing point curve. On the left hand side of the eutectic composition it crosses the melting point curve twice, and on the right hand side of the eutectic it again crosses the melting point curve. Near the eutectic composition the supersolubility curve reaches a minimum, and for mixtures containing from 70 to 90 per cent. of benzylaniline the

supersolubility curve is very flat, the temperatures of spontaneous crystallisation for these mixtures only varying by about 2°.

(2) *The Refractive Indices of Mixtures.*—An attempt was now made to verify the supersolubility curve just obtained by observing the sudden change in the index of refraction which takes place on the curve. This method has been used before to obtain the supersolubility curve for mixtures of salol and betol and for various aqueous solutions of salts, &c.*

The liquid mixtures were heated and placed in the trough of the inverted goniometer and their refractive indices were determined as they cooled by the method of total reflection within a dense glass prism immersed in the liquid.

With the aqueous solutions examined in this manner it was found that the refractive index rose steadily till the labile temperature was reached. Here a dense shower of crystals occurred, which soon settled at the bottom of the goniometer trough, the refractive index afterwards falling continually as the temperature fell.

The mixtures of azobenzene and benzyaniline were examined in this manner from the time when the warm mixture was first placed in the trough until the dense shower occurred at the labile temperature. As with the mixtures of salol and betol already examined, it was almost impossible to determine the refractive index beyond this point owing to the density of the shower, the crystals remaining suspended in the liquid instead of sinking to the bottom of the trough as with the aqueous solutions of salts, and thus rendering the mixtures almost opaque.

The mixtures of azobenzene and benzyaniline examined contained from 50 to 100 per cent. of benzyaniline. In these it was found that the index rose gradually and regularly as the temperature fell, until the dense labile shower of crystals occurred. Mixtures containing more than 50 per cent. of azobenzene were not examined, as they were somewhat viscous, and consequently intense concentration streams arise, which cause irregularities in the index-temperature curves, and also because their high temperatures of spontaneous crystallisation render them unsuitable for use in the goniometer trough. As the mixtures cooled in the trough they were stirred continually by means of a small platinum vane driven by an electric motor.

The liquid mixtures being somewhat deep red in colour, it was found that the monochromatic light of the sodium flame was nearly absorbed, and that the edge of the shadow denoting total internal reflection could hardly be seen. White light was therefore used to illuminate the prism, and a piece of

* 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 322; 'Journ. Chem. Soc.,' 1908, vol. 93, i, p. 384.

red glass was held in front of the eye-piece of the telescope to cut off light of other colours. The refractive index of the liquid mixtures is thus determined for red light. The shadow denoting total internal reflection obtained in this way is quite sharp and distinct. The shower of crystals occurring in the mixtures at the labile temperature is always accompanied by a considerable rise in temperature. The following are the general results of the experiments on the refractive indices of mixtures of azobenzene and benzylaniline.

Experiment 1.—Azobenzene = 50 per cent.
Benzylaniline = 50 „

The index rose from 1·62022 at 61° to 1·63237 at 35°. A dense shower occurred at 35° and the temperature rose to 38°.

Experiment 2.—Azobenzene = 47·5 per cent. approx.
Benzylaniline = 52·5 „ „

The index rose from 1·61684 at 63° to 1·63146 at 35°. A dense shower occurred at 33·5°, the temperature rising to 38°.

Experiment 3.—Azobenzene = 45 per cent. approx.
Benzylaniline = 55 „ „

The index rose from 1·61432 at 66° to 1·63115 at 33°. A very dense shower occurred at 32°, the temperature rising to 36°.

Experiment 4.—Azobenzene = 39·995 per cent.
Benzylaniline = 60·005 „

The index rose from 1·61421 at 60° to 1·62941 at 31°. A shower of crystals occurred at 31° and the temperature rose to 33°.

Experiment 5.—Azobenzene = 35 per cent.
Benzylaniline = 65 „

The index rose from 1·61224 at 61° to 1·62864 at 27°. A shower of crystals occurred at 26·5 and the temperature rose to 28°·5.

Experiment 6.—Azobenzene = 30 per cent.
Benzylaniline = 70 „

The index rose from 1·61202 at 55° to 1·62937 at 22°. A slight shower began to form spontaneously at 22° and became gradually denser without change of temperature.

Experiment 7.—Azobenzene = 30 per cent. approx.
Benzylaniline = 70 „ „

The index rose from 1·61054 at 60° to 1·62892 at 22°. A shower of crystals occurred at 22° and the temperature rose to 25°.

Experiment 8.—Azobenzene = 25 per cent.
Benzylaniline = 75 „

The index rose from 1·60946 at 56° to 1·62868 at 20°·5. A shower occurred at 20°·5, the temperature rising to 25° and the index falling. At 21° the index had fallen to 1·62627.

Experiment 9.—The same mixture was used as in Experiment 8. The index rose from 1·61174 at 53° to 1·62622 at 21°. A dense shower occurred at 20°·5, but no more readings for the index were possible. The temperature rose to 24°·5.

Experiment 10.—Azobenzene = 20·045 per cent.
Benzylaniline = 79·955 „

The index rose from 1·60344 at 58° to 1·62566 at 19°. A shower of crystals occurred at 19° and the temperature rose to 25°. The index fell again during the shower and reached 1·62397 at 21°·5.

Experiment 11.—Azobenzene = 17·256 per cent. approx.
Benzylaniline = 82·744 „ „

The index rose from 1·60653 at 56° to 1·62428 at 18°·2. A dense shower of crystals occurred at this temperature and no more readings were possible. The temperature rose to 27°.

Experiment 12.—Azobenzene = 14·886 per cent.
Benzylaniline = 85·114 „

The index rose from 1·61060 at 44° to 1·62282 at 18°·2. A shower of crystals occurred at this temperature and the index fell with rise of temperature, reaching 1·62165 at 23°.

Experiment 13.—Azobenzene = 10·003 per cent.
Benzylaniline = 89·997 „

The index rose from 1·60235 at 57° to 1·61895 at 21°. A dense shower occurred at 21°, the temperature rose to 29° and the index fell to 1·61866 at this temperature.

Experiment 14.—Azobenzene = 0 per cent.
Benzylaniline = 100 „

The index rose from 1·59324 at 64° to 1·60999 at 29°·2. Crystals first appeared at 30° and a dense shower occurred at 29°·2, the temperature then rising to 35°.

From experiments 1, 4, 5, 6, 8, 10 and 13, in which the exact composition of the mixtures is known, it is possible to ascertain the refractive index of any given mixture at any temperature. The results of all these experiments, taken together, may be expressed by curves drawn with concentrations as abscissæ and temperatures as ordinates, the refractive index being constant for each curve. Such curves were drawn for the following values of index:—1·608, 1·610, 1·612, 1·614, 1·616, 1·618, 1·620, 1·622, 1·624, 1·626, 1·628, 1·630. They were found to be very approximately straight lines, equidistant and parallel to each other, and inclined to the concentration axis at an angle of 50°, the scale chosen being such that 10 per cent. on the concentration axis corresponds to 8° on the temperature axis. Now, if a line be drawn on the concentration-temperature diagram perpendicular to these lines of constant index, and, therefore, inclined at an angle 40° to the concentration axis, the refractive

index of any mixture, as it cools, may be measured along this line just as the temperature is measured along the vertical axis.

The curves of constant index are shown on the diagram, and from these it is possible to plot the whole series of observations of refractive indices obtained in the above experiments. (See p. 363.)

These experiments give a number of curves, numbered 1 to 14 on the diagram, the number of the curve corresponding to the number of the experiment. The curves show slight irregularities, especially at high temperatures. These irregularities are probably due to concentration-streams, which are particularly marked when the liquid mixture is first introduced into the goniometer trough.

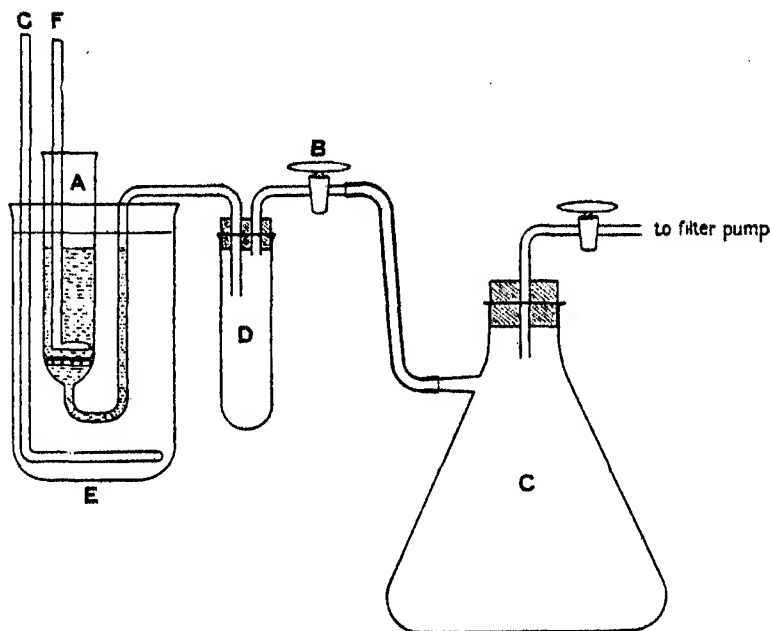
On the whole, however, the curves go straight down the diagram and show very little variation in concentration as the mixtures cool, until the labile shower occurs at points which lie very approximately on the supersolubility curve already obtained by the method of sealed tubes. These results, obtained from the refractive indices of the mixtures, therefore confirm those already obtained from the experiments with sealed tubes, by which the position of the supersolubility curve was first established. In two or three of the experiments, in which it was possible to trace the refractive index after the labile shower had begun, it was found that the index attained a maximum value on the supersolubility curve and then fell again with rise of temperature and approached the freezing point curve. This behaviour is seen in experiments 10, 12 and 13. In general, however, it is not possible to trace the change of index with any certainty after the shower has occurred, the shower being usually so dense as to render the mixture opaque.

The crystals which first separate from the mixtures during the showers were examined from time to time under the microscope, but no definite conclusions as to their nature could be drawn from the observations. The crystals were always needles and showed straight extinction. Their angles were never measurable under the microscope. An interference figure was usually visible; sometimes both optic axes were seen with the bisectrix normal, and sometimes only one optic axis was visible, surrounded by rings, the birefringence being always positive.

Nature of the Crystals Separating on the Supersolubility Curve.

The supersolubility curve having been determined by the above experiments, an attempt was now made to ascertain the composition of the crystals which first form spontaneously on the supersolubility curve for various mixtures. In order to do this for any mixture it is necessary to separate the first crystals which form in the labile shower.

For this purpose the following apparatus was devised by Prof. Bowman, and is shown in the figure:—



A wide tube A is drawn out at the lower end to form a U-tube, the end of which is bent again and passes through a cork into the tube D. This U-tube is immersed in a large water-bath E. Another tube passes through the cork of the tube D and connects it with the vacuum flask C and air pump. By means of the tap B this connection may be opened or closed at will. At the bottom of the tube A is a porcelain filter-plate covered with a filter-paper.

The liquid to be experimented upon is placed in the U-tube at a high temperature, the water-bath E having been previously heated. The liquid in the U-tube is stirred continuously and steadily by means of a plunging stirrer F, driven by an electric motor. By far the greater part of the liquid mixture is contained in the wide part A of the U-tube, and is allowed to cool very slowly in the water-bath. As soon as the liquid reaches the labile temperature a shower of crystals begins to form in the tube A. The tap B is then immediately turned and the liquid mixture sucked off into the tube D, leaving the first crystals that form in the shower dry and free from mother liquor upon the filter-paper in A. A thermometer was placed in the water-bath, which was kept stirred throughout the experiment by the glass stirrer G. The melting point of the crystals left in the tube A was then obtained

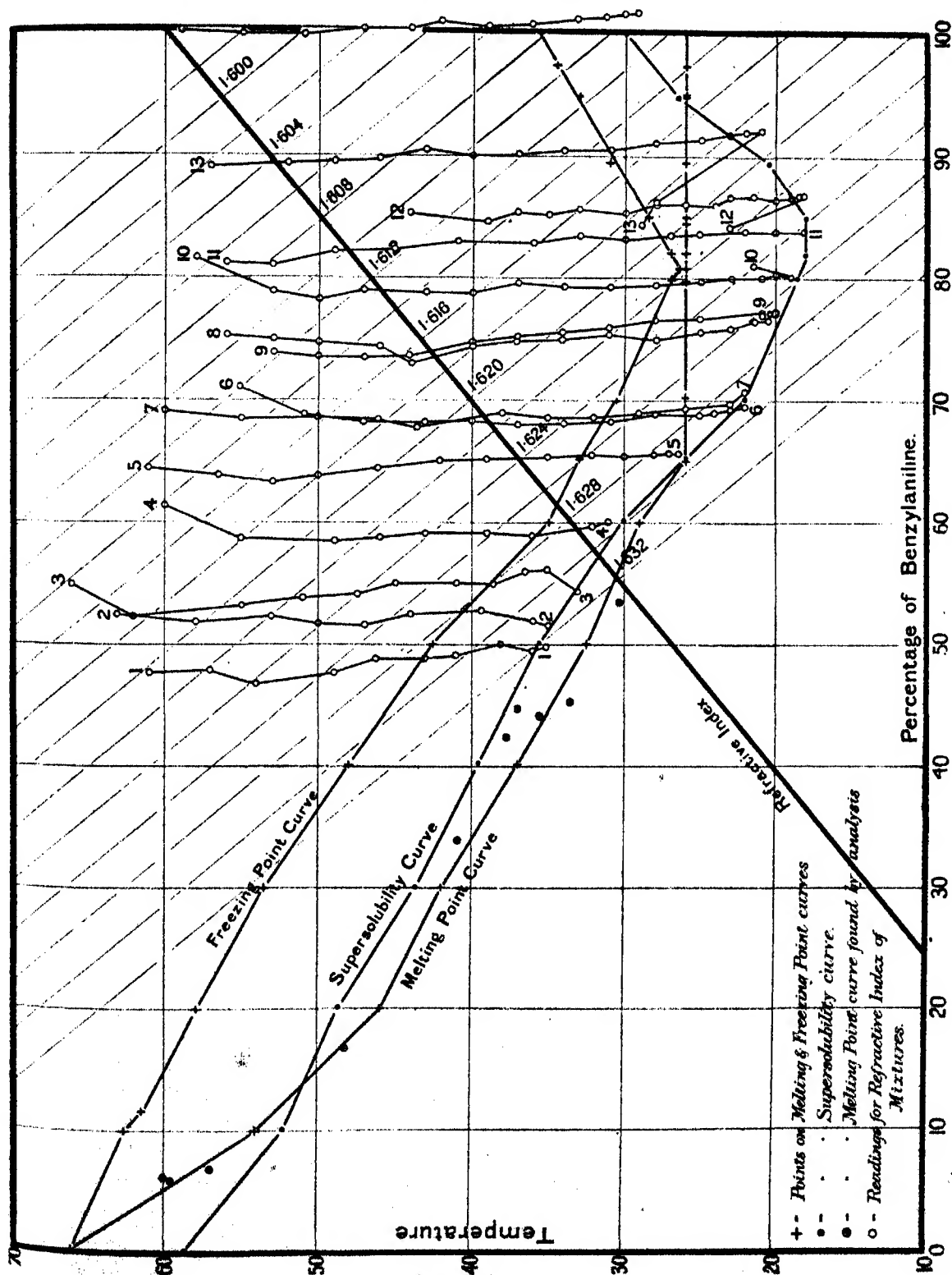
in a capillary tube attached to the bulb of a thermometer in the usual manner. The capillary tubes used in these experiments were examined from time to time under the microscope, by which means the first signs of melting at the edges of the crystals were easily detected.

It is necessary to catch the shower in the U-tube at once so as to separate the first crystals that form. If the tap B connecting the tube A with the vacuum flask is not turned immediately the first crystals appear, too much solid forms in A, and the filter-paper is left with a large mass of crystals on it, instead of only the first few crystals which form. Sometimes the liquid mixture solidifies at the narrow upper end of the U-tube when running off into D, and this prevents the mother liquor from being properly drawn away from the first crystals on the filter. Usually, however, if the mixture is very carefully watched, it is possible to isolate the first crystals of the labile shower, and though they are always extremely small and brittle needles they have clear sharp edges, and appear quite free from the mother liquor. The following results were obtained with this apparatus, the crystals being always examined in capillary tubes as stated above.

1. Mixture containing 40 per cent. benzyaniline; 60 per cent. azobenzene. —This mixture was placed in the U-tube at about 80° and cooled slowly in the water-bath whilst it was stirred continuously. It crystallised spontaneously very suddenly at a somewhat high temperature, *i.e.* 39.5°, and it was found extremely difficult to draw off the mother liquor with sufficient rapidity to ensure the first crystals that formed being left clean on the filter. The experiment had therefore to be repeated several times before any definite result was obtained. At length, however, the liquid was drawn off, leaving a few of the very first crystals of the labile shower on the filter. When examined in a capillary tube these showed a definite melting point at 39°. The diagram shows that mixed crystals whose melting point is 39° have a composition of approximately 35 per cent. benzyaniline, 65 per cent. azobenzene. This, therefore, appears to be the composition of the crystals separating spontaneously from a liquid mixture containing 40 per cent. benzyaniline and 60 per cent. azobenzene.

Another experiment with the same liquid mixture yielded a larger crop of crystals on the filter. These appeared to be quite dry and free from mother liquor, but the melting point of different samples did not appear to be quite constant, the crystals melting at 39°, 38.5°, and 39.5°. The composition of these crystals would appear therefore to vary from 36 per cent. benzyaniline with 64 per cent. azobenzene, to 34 per cent. benzyaniline with 66 per cent. azobenzene.

2. Mixture containing 50 per cent. benzyaniline; 50 per cent. azobenzene.



—This mixture was placed in the U-tube apparatus at 70°. A shower of crystals began to form at 35°, and the rest of the liquid was driven into the tube D leaving the first crystals of the shower dry on the filter. Three samples of these were examined in capillary tubes and found to melt at 34°, 35°, and 34·5°, and their composition therefore probably varies from 44·5 per cent. benzy laniline with 55·5 per cent. azobenzene, to 46·5 per cent. benzy laniline with 53·5 per cent. azobenzene. Mixed crystals of approximately this composition appear therefore to separate spontaneously from a liquid mixture containing 50 per cent. azobenzene with 50 per cent. benzy laniline.

3. Mixture containing 65 per cent. benzy laniline ; 35 per cent. azobenzene. —This mixture was placed in the U-tube at 70° and stirred steadily. A shower of crystals began to form at the labile temperature 26°, and the first crystals were easily separated, since in this mixture the shower does not form so suddenly throughout the liquid as is the case with mixtures containing a higher percentage of azobenzene. Three samples were examined in capillary tubes and found to melt at temperatures between 28° and 29°, their composition therefore varying from 59·5 per cent. benzy laniline with 40·5 per cent. azobenzene, to 61 per cent. benzy laniline with 39 per cent. azobenzene.

4. Mixture containing 75 per cent. benzy laniline ; 25 per cent. azobenzene. —This mixture was placed in the U-tube at 70°. At 20° a shower began to form in the tube. This was separated from the rest of the liquid and the crystals examined in capillary tubes. They were found to start melting at 26°. The capillary tubes must therefore contain some mixed crystals of constitution 65 per cent. benzy laniline, 35 per cent. azobenzene, which melt at 26°, and give the limit beyond which mixed crystals are not formed, the rest of the mixture in the capillary tubes being presumably pure benzy laniline. Another experiment was made with the same mixture by the same method. In this experiment it was noticed that the shower began to form at 20° with a very few small needle-shaped crystals and radial groups, and a thick shower did not come down immediately. These small crystals were separated in the usual way and washed with a few drops of benzene while still on the filter in the U-tube, the benzene being at once drawn off by means of the filter pump. They were then examined under the microscope and placed in capillary tubes. Some of them were pure white in colour, and some showed traces of the orange colour of the azobenzene. The colourless crystals in the capillary tubes when slowly heated in a water-bath showed no sign of melting till the temperature was raised to 35·5°, the melting point of pure benzy laniline. The crystals which showed some sign of the azobenzene colour, however, all began to melt very slightly at 26°. It would therefore appear that the first crystals to

form spontaneously from a mixture containing 75 per cent. benzylaniline and 25 per cent. azobenzene consist of a mixture of pure benzylaniline and mixed crystals containing 35 per cent. azobenzene with 65 per cent. benzylaniline.

5. Mixture containing 83.5 per cent. benzylaniline; 16.5 per cent. azobenzene.—This mixture also was placed in the U-tube at 70° and stirred as it cooled from this temperature to 18° in 3½ hours. A slight shower commenced at 18°, and was immediately separated from the rest of the liquid. The crystals thus obtained showed some sign of the colour of the azobenzene, and examined in capillary tubes began to melt at 26°. They therefore probably contain some proportion of the mixed crystals of composition 35 per cent. azobenzene, 65 per cent. benzylaniline. The experiment was repeated again in the same way, but in this case the first crystals separating at 18° were washed several times with benzene while still on the filter in the U-tube. When examined in capillary tubes these crystals did not melt till the temperature was raised to 35.5°, and under the microscope they appeared to be pure white in colour. Pure benzylaniline, therefore, apparently first separates spontaneously from this mixture, and if the crystals are freed from mother liquor by washing with benzene, the melting point of pure benzylaniline is attained.

6. Mixture containing 90 per cent. benzylaniline; 10 per cent. azobenzene.—This mixture was placed in the U-tube at 60° and cooled very slowly. A slight shower commenced at 20.5°, the crystals of which were easily separated by means of the vacuum pump. The crystals were small radial groups. They were washed with benzene whilst still on the filter in the U-tube, the benzene being at once drawn off with the vacuum pump. These crystals were colourless, and when placed in capillary tubes melted at 35.5°, the melting point of pure benzylaniline. If, however, the crystals were not washed with benzene before they were examined, they appeared to be yellowish in colour, and showed signs of melting at 26°. This would be accounted for by the presence of the mother liquor adhering to the crystals.

7. Mixture containing 94.74 per cent. benzylaniline; 5.26 per cent. azobenzene.—This mixture, placed in the U-tube apparatus at about 60° and cooled in the same manner, gave a shower of crystal needles and radial groups at the labile temperature, 26.5°. These were easily separated since the shower takes some time to thicken. They were washed two or three times with a few drops of benzene whilst still on the filter in the U-tube, and when placed in capillary tubes did not melt until the temperature was raised to 35.5°. They were also quite colourless, and were therefore apparently pure benzylaniline.

From these experiments it will be seen that in general, with mixtures which contain a larger amount of azobenzene than the eutectic composition, the crystals which first separate spontaneously on the supersolubility curve contain a larger percentage of azobenzene than does the original mixture. In general, for such mixtures, the supersolubility curve was found to lie above the melting-point curve. From the results obtained, therefore, with these mixtures, we see that the composition of the first crystals separating spontaneously at any point on the supersolubility curve is very approximately given by drawing a line from this point parallel to the concentration axis to meet the melting point curve. The point in which the line so drawn meets the melting point curve gives the approximate composition of the crystals which have first separated from the mixture under examination. With mixtures which contain a larger amount of benzyaniline than the eutectic composition, however, the crystals which first separate have been shown above to be pure benzyaniline.

In the case of mixtures which approximate to the eutectic composition, it has been shown that the crystals first separating are frequently a mixture of pure benzyaniline with mixed crystals of 35 per cent. azobenzene and 65 per cent. benzyaniline, the limiting composition.

Thin Sections Cut from Mixtures of Azobenzene and Benzyaniline.

An attempt was made to study the structure of a few of the solidified mixtures under the microscope. To do this thin sections were made from the mixtures that had solidified completely in glass tubes. The glass tube was broken and the solid rod of mixture removed. Discs and longitudinal sections were cut from this with a fret-saw, and then ground on ground-glass plates until they were sufficiently thin and transparent for microscopic examination.

Sections were cut in this way from the following mixtures:—

1. Mixture containing 30 per cent. azobenzene and 70 per cent. benzyaniline.—This mixture crystallised spontaneously while shaken continually in a sealed tube. When ground into thin sections this showed a large quantity of yellow rod-shaped crystals small in size, and distributed irregularly all over the sections, also some radial groups growing from centres. These are probably mixed crystals of the limiting composition, i.e. with 35 per cent. azobenzene and 65 per cent. benzyaniline. The rest of the section is filled up with large colourless crystals of presumably pure benzyaniline. Under the microscope these exhibit ophitic structure and extinguish in large patches all over the slide, and have probably grown at rest after the shower of mixed crystals has occurred.

This mixture was not ground into thin sections until it had been solid in a glass tube for several weeks.

2. Mixture containing 10 per cent. azobenzene and 90 per cent. benzyaniline.—This mixture also crystallised spontaneously while shaken continually in a sealed tube. This

section showed a mass of small white crystals, with small yellow crystals filling up the spaces between them. No regular arrangement could be observed, and the crystals were all more or less rod shaped.

After this section had been left for four weeks at a temperature of about 10° , it was observed that a new growth was taking place at the surface of the section. Sharply-formed thin rods could be seen quite clearly, growing out of the solid, the rods being both yellow and white in colour.

3. Mixture containing 5 per cent. azobenzene and 95 per cent. benzyaniline.—Crystallised spontaneously at rest. Sections cut from this mixture showed large, pure white crystals of benzyaniline, growing as large compact masses which extinguish together, and also as large radial groups. Small rod-shaped yellow crystals fill up the gaps.

After these sections had been kept for a few weeks at about 10° , they also showed distinct signs of segregation. Under the high power of the microscope thin rods can be seen growing up all over the surface of the sections.

4. Mixture containing 5 per cent. azobenzene and 95 per cent. benzyaniline.—Crystallised spontaneously while shaken continually. Thin sections cut from this mixture have much the appearance of the sections of (3) above, but the crystals are much smaller and arranged irregularly all over the slide.

After keeping these sections for some weeks at a low temperature, they also show thin rods growing up over their surface when examined under the high power of the microscope.

The study of the thin sections seems to indicate that, in mixtures weak in azobenzene, changes take place in the solid solutions when they are given sufficient time. It will be seen that this breaking up, or segregation, does not appear to occur in sections (1) above, but it is to be noted that these sections were not ground until the mixture had been solid for some weeks at the temperature of the room, *i.e.* about 10° . It is probable, therefore, that the change had already taken place before the section was ground, and that equilibrium had already been established between the solid solution and the benzyaniline at this temperature. The remaining sections were ground within a few hours of having solidified, so that the structures observed would correspond to equilibrium at the temperatures given by the supersolubility curve; since, presumably, sufficient time had not elapsed for them to attain equilibrium at the temperature of the room. Hence, changes begin to show themselves later in the solid section, readjustment of the components of the mixed crystals taking place until equilibrium is finally established at the ordinary air temperature.

After the lapse of three winter months these sections were all examined again under a high power. It was found that they had all undergone considerable further change, and very little of their original structure was recognisable. Sections (1), which three months before showed no sign of breaking up, had now entirely changed, and were riddled with minute crystal needles, both yellow and colourless. It was also noted that in

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several of the sections the small newly formed needles were arranged in parallel positions over the surface.

Conclusion.

The results obtained in this research may be thus summarised:—

1. The freezing and melting point curves for mixtures of azobenzene and benzylaniline have been determined, and it has been shown that these substances possess a minimum or eutectic point at 26° for the mixture containing 19 per cent. azobenzene and 81 per cent. benzylaniline, and form a series of mixed crystals on one side only of the eutectic, viz., that with excess of azobenzene. This is, therefore, a limiting case of Roozeboom's Type 5, in which two substances, A and B, possess freezing and melting point curves which exhibit a minimum eutectic point, and form two series of mixed crystals, *i.e.* mixed crystals containing excess of A, and mixed crystals containing excess of B.

2. The melting point curve has been confirmed by actual analysis of the mixed crystals.

3. The supersolubility curve, or curve of spontaneous crystallisation, has been determined for these mixtures by two methods: (1) by noting the temperature at which a liquid mixture of known composition crystallises spontaneously in a sealed tube; (2) by noting the temperature at which a known liquid mixture attains its highest refractive index, and gives a dense labile shower when placed in the trough of the inverted goniometer. By these methods it has been shown that each mixture possesses a definite temperature of spontaneous crystallisation.

The supersolubility curve shows a minimum for liquids having approximately the eutectic composition, and runs approximately parallel to the freezing point curve. It crosses the melting point curve three times as shown in the diagram.

4. The nature of the mixed crystals which first separate spontaneously from any liquid mixture on the supersolubility curve has been investigated. The composition of such crystals has been determined by separating them from their mother liquor and finding their melting points.

5. A few thin sections have been ground from the solid mixtures in the neighbourhood of the eutectic, and their structures examined. These structures do not appear to be permanent, and after the lapse of some months they had completely changed, new crystal needles having appeared all over the sections. These changes, however, appear to be very gradual and to take place with change of temperature.

The analysis of these mixtures was carried out in the Balliol and Trinity Laboratory, Oxford, by permission of Messrs. Nagel and Hartley, to whom I am much indebted for their kind help and advice. I also take this opportunity of expressing my grateful thanks to Principal H. A. Miers and to Prof. Bowman for the helpful criticism and advice they have given me throughout the course of this research.

On the Improbability of a Random Distribution of the Stars in Space.

By F. W. DYSON, M.A., F.R.S.

(Received July 9, 1910.)

In a recent paper* Prof. Karl Pearson obtains the following results:—

(i) If $P = \log_{10}\pi$ when π denotes the parallax of a star, and σ_P be the standard deviation, or square root of the mean square deviation of a series of values of P from the mean; then, for a uniform distribution of stars in space, $25\sigma_P^2 = 0.5240$.

(ii) If \bar{m} be the mean magnitude of all stars down to and including those of magnitude m_0 , then

$$\bar{m} = m_0 - 0.7238, \text{ and } \sigma_m^2 = 0.5240.$$

1. The first of these results is compared with the values of $25\sigma_P^2$, obtained from a list of 72 parallaxes of stars given in Newcomb's 'The Stars: A Study of the Universe,' and with those of 163 stars given in 'Trans. Yale Univ. Observatory,' Vol. II.

For Newcomb's stars $25\sigma_P^2 = 4.22$,
and for the Yale stars, $25\sigma_P^2 = 3.11$.

The inference that these stars are not evenly distributed in space may be obtained more easily. Among the Yale stars there are ('Trans. Yale Univ. Observatory,' Vol. II, p. 205)—

17 stars with parallax $0.14''$ to $0.20''$
and 30 „ „ „ $0.07''$ „ $0.13''$.

With a uniform distribution 8×17 , or 136 stars, may be expected to have parallaxes from $0.07''$ to $0.10''$, if there are 17 with parallaxes from $0.14''$ to $0.20''$; and a larger number than 136 between the limits $0.07''$ and $0.13''$.

* 'Roy. Soc. Proc., A, vol. 84, pp. 47—70.

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But no inferences can be drawn from these figures as to the distribution of the stars in general. These particular stars were selected for observation largely on account of their great proper motions. This criterion was successful in leading to the discovery of 17 very near stars.

2. The formulæ $\bar{m} = m_0 - 0.7238$, and $\sigma_m^2 = 0.5240$, are immediately deducible from the proposition that for a uniform distribution of stars, and assuming no absorption of light, the total number of stars down to magnitude m is given by

$$\Sigma m = C(2.512)^m = C(3.99)^m.$$

In this well-known formula, 2.512 is the ratio of the amount of light received from two stars which differ by one magnitude. A formal proof of the formula may be given as follows:—

Let $\phi(m)$ be the number of stars contained in unit volume, of magnitude m or brighter, as seen from unit distance. A thin spherical shell of radius r will contain $\phi(m) \cdot 4\pi r^2 dr$ of such stars.

Now if a star is of magnitude m at unit distance, its magnitude at distance r is $m + 5 \log_{10} r$. Thus $\phi(m - 5 \log_{10} r) \cdot 4\pi r^2 dr$ equals the number of stars in the shell which, seen from the centre, appear to be of magnitude m .

Therefore the total number of stars down to magnitude m is given by

$$\Sigma m = \int_0^\infty \phi(m - 5 \log_{10} r) \cdot 4\pi r^2 dr.$$

$$\begin{aligned} \text{Thus} \quad \Sigma m + 1 &= \int_0^\infty \phi\left(m - 5 \log_{10} \frac{r}{k}\right) \cdot 4\pi r^2 dr \\ &= k^3 \Sigma m, \quad \text{where} \quad 5 \log_{10} k = 1. \end{aligned}$$

Therefore

$$\Sigma m = C(3.99)^m.$$

3. Writing this in the form $\Sigma m = C e^{\lambda m}$,

$$\bar{m} \Sigma m_0 = \int_0^{\Sigma m_0} m d \Sigma m = m_0 \Sigma m_0 - \int_{-\infty}^{m_0} \Sigma m \cdot dm = (m_0 - \lambda^{-1}) \Sigma m_0,$$

or

$$\bar{m} = m_0 - \lambda^{-1} = m_0 - 0.7238;$$

and, similarly,

$$\sigma_m^2 = \lambda^{-2} = 0.524.$$

Thus Prof. Pearson's formulæ follow directly from the law $\Sigma m = C(3.99)^m$, and no assumption is made with regard to the form of $\phi(m)$. The assumption is, however, made that the stars extend to infinity and that there is no absorption of light in space.

4. Now in the table quoted by Prof. Pearson from the 'Harvard Annals,' the numbers of stars as far as magnitude 7.25 roughly agree with the formula

$$\Sigma m = C(3.222)^m,$$

from which $\bar{m} = m_0 - 0.855$ and $\sigma_m = 0.731$ are deducible, values which agree with those found by Prof. Pearson.

5. It does not seem to me that Burnham's catalogue of double stars can be used as a basis for a discussion of the departure of the actual distribution of the stars from a random distribution. As far as magnitude 9.5, Hussey and Aitken have made systematic search for all double stars. Beyond this magnitude no systematic search has been made. Further, the definition of a double star is a very elastic one. Thus on page 1 of Burnham's catalogue, α Andromedæ (2.0) with a companion of magnitude 11.2 at a distance of 65'' is counted as a double star. Two faint stars of magnitude 9.0 or 10.0 at this distance would not be classified as double, and the photographs taken for the Astrographic Catalogue contain many such stars.

The Conditions Necessary for Discontinuous Motion in Gases.

By G. I. TAYLOR, B.A., Trinity College, Cambridge.

(Communicated by Prof. Sir Joseph Larmor, Sec. R.S. Received July 11, 1910.)

The possibility of the propagation of a surface of discontinuity in a gas was first considered by Stokes* in his paper "On a Difficulty in the Theory of Sound." This paper begins with a physical interpretation of Poisson's integral of the equation of motion of a gas in one dimension. The integral in question is $w = f\{z - (a + w)t\}$; and it represents a disturbance of finite amplitude moving in a gas for which the velocity of propagation of an infinitesimal disturbance is a ; w is the velocity of the gas in the direction of the axis z . It is shown that the parts of the waves in which the velocity of the gas is w travel forward with a velocity $a + w$, and that there is in consequence a tendency for the crests to catch up the troughs. After a certain time, and at a certain point in space, the value of $\partial w / \partial z$ will become negatively infinite; a discontinuity will then occur, and Poisson's integral will cease to apply.

Stokes then leaves the subject of oscillatory waves and proceeds to consider whether it is possible to maintain a sharp discontinuity in a gas which obeys Boyle's law ($p = a^2 \rho$). His argument, slightly modified by Lord Rayleigh, is as follows:—

Suppose that a travelling discontinuity can exist. Give the whole gas

* 'Phil. Mag.,' 1848, vol. 33, p. 349; 'Collected Papers,' vol. 1.

such a motion that the discontinuity is brought to rest. Consider then a gas which is moving with uniform velocity u_1 up to a discontinuity. At this point the velocity suddenly changes to u_2 ; and the gas moves on uniformly at this speed. Let ρ_1 and ρ_2 be the corresponding densities, p_1 and p_2 the corresponding pressures.

The equation of continuity of mass is

$$\rho_1 u_1 = \rho_2 u_2. \quad (1)$$

The equation of conservation of momentum is

$$p_1 - p_2 = a^2 \rho_1 - a^2 \rho_2 = \rho_1 u_1 (u_1 - u_2). \quad (2)$$

If u_1 and ρ_1 be given, these two equations determine u_2 and ρ_2 .

Against this theory, however, Lord Rayleigh* raised the objection that the equation of energy, $\frac{1}{2} u_1^2 - \frac{1}{2} u_2^2 = a^2 \log \rho_1 - a^2 \log \rho_2$, cannot, in general, be satisfied simultaneously with (1) and (2).

In a recent note† he adds a remark that it is possible that energy might be lost at the discontinuity, but it cannot be supposed that energy is gained. Lord Rayleigh further points out that the energy lost must be converted into heat, and that this complication must be taken into account. This has been done by C. V. Burton‡ and by Hugoniot,§ but their equations have the same disadvantage as those of Stokes, in that they contain no indication that the motion represented by them is irreversible.

In the case considered by Stokes it is evident that the motion is irreversible; in fact, it is only the front of a compression that can possibly travel unchanged. For, if for an instant the sharp discontinuity were to disappear, leaving a small transition layer in which the velocity might vary continuously from u_1 to u_2 , then the back part of the layer would travel forward relatively to the front part with a velocity $u_1 - u_2$. Hence if u_1 exceeds u_2 any such transition layer will become obliterated owing to the greater velocity behind, and the discontinuity will thus be maintained. This is the case of the front of a wave of condensation. If, however, the wave is a wave of rarefaction, that is, if u_1 is less than u_2 , then the layer of transition will get wider, and the sharp discontinuity will not be re-established.

The object of this paper is to discuss in detail what actually does occur at a discontinuity, and to determine, in the general case of a gas whose characteristics are known, whether a discontinuity obtained by the method

Stokes is a physically possible feature.

* 'Theory of Sound,' vol. 2, p. 41.

† 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 449.

‡ 'Phil. Mag.,' 1893, vol. 35, p. 317.

§ See Lamb's 'Hydrodynamics,' note on p. 466, 3rd edition

It is evident that a plane of absolutely sharp or mathematical discontinuity cannot occur in any real gas. When, owing to change of type, there is a sudden compression or rarefaction of the material in crossing any boundary, modified physical laws must come into operation whose effect is to prevent abrupt discontinuity from being formed. Some clue to the nature of the processes involved in this case is afforded by the kinetic theory of gases; for when the change in velocity is very sudden, the molecules which are moving faster will penetrate among those which are moving more slowly, and an irreversible redistribution of velocities will ensue. This suggests that heat conduction and viscosity are, in the case of a real gas, the causes of the production of dissipative heat; it will be shown that under certain conditions they are also sufficient to produce permanence of type in the layer of transition.

Consider a continuous disturbance of permanent type in a gas whose characteristic equations are known. Give the whole system such a velocity that the disturbance is brought to rest; the motion is then steady.

Let A and B be two planes which move with the gas, and let p', ρ', u', E' , and p, ρ, u, E , be the pressure, density, velocity, and internal energy of unit mass of the gas at A and B respectively. Since θ , the temperature, is a function of p and ρ , and E is a known function of p, ρ , and θ , therefore E may be regarded as a function of independent variables p and ρ .

The equation of continuity of matter is

$$\rho' u' = \rho u = \omega. \quad (3)$$

The rate of gain of momentum between A and B is $\omega(u - u')$. The equation of momentum for the gas between A and B is therefore

$$(p + X) + \omega u = (p' + X') + \omega u', \quad (4)$$

where X and X' are the viscous normal forces which act over the planes B and A respectively.

The work done on the gas between A and B in a small interval of time dt is

$$(p' + X') u' dt - (p + X) u dt.$$

The increase of its kinetic energy in time dt is

$$\frac{1}{2} \omega (u^2 - u'^2) dt.$$

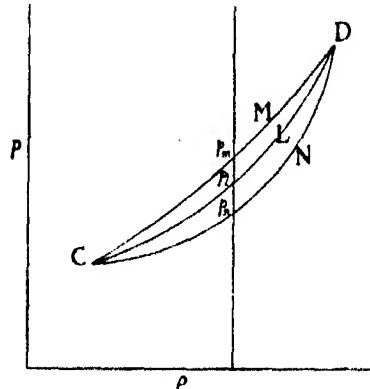
The increase in internal energy in the same time is $(E - E') \omega dt$.

The amount of heat conducted away from the mass of gas between A and B in time dt is $\omega(\xi - \xi') dt$, where $\omega\xi$ and $\omega\xi'$ are the rates at which heat, measured in mechanical units, is conducted across the planes B and A.

The equation of energy for the gas between A and B is therefore

$$(p + X) u + \frac{1}{2} \omega u^2 + \omega(E + \xi) = (p' + X') u' + \frac{1}{2} \omega u'^2 + \omega(E' + \xi'). \quad (5)$$

Since E is a function of p and ρ and $u = \omega/\rho$, the state of the gas at any time may be completely represented by a point in a plane diagram such as is annexed; pressure is represented by the ordinates and density by the



abscissæ. If C and D are the points which represent the state of the gas at the two ends of the transition layer in which the velocity changes from u_1 to u_2 , then the state of the gas along that layer are represented by the points on some curved line L joining C and D . It will be possible by means of equations (4) and (5) to determine values of X and ξ so that any given line joining C and D may represent the state of the gas in the transition layer; but the motion so represented will not be thermodynamically possible unless the coefficients of conduction and viscosity are both positive. If x represents distance in the direction in which the gas is travelling, these conditions become

X and $\partial u/\partial x$ must have opposite signs,

ξ and $\partial \theta/\partial x$ must have opposite signs.

Hence at the front of a condensation X is positive and ξ is negative while for a rarefaction X is negative and ξ is positive.

Construct curves M and N to represent the relations obtaining between p and ρ when $X = 0$ and when $\xi = 0$ respectively. Let p_m , p , and p_n represent the pressures at points on M , L , and N corresponding to a particular value ρ of the density.

The equation to M is obtained by dropping X from (4), and is

$$p_m + \omega u = p_1 + \omega u_1,$$

and since (4) gives

$$(p + X) + \omega u = p_1 + \omega u_1,$$

therefore

$$p_m = p + X.$$

Similarly it can be shown that $E_n = E + \xi$.

In a condensation therefore $p_m > p$ and $E_n < E$, and in a rarefaction $p_m < p$ and $E_n > E$.

Also $E_n - E = (\theta_n - \theta)C_v$ where C_v is the specific heat at constant volume; and $p_n - p$ must be of the same sign as $\theta_n - \theta$; hence in a condensation $p_m > p > p_n$, and in a rarefaction $p_m < p < p_n$.

Now the equations to the lines M and N depend only on the relations which exist between pressure, density, temperature, and internal energy, that is on the characteristic equations of the gas, and not at all on its viscosity or its conductivity; for if either X or ξ is small the other can be eliminated.

Hence if a discontinuity is specified by the equations

$$u_1 \rho_1 = u_2 \rho_2 = \omega,$$

$$p_1 + \omega u_1 = p_2 + \omega u_2,$$

$$p_1 u_1 + \frac{1}{2} \omega u_1^2 + \omega E_1 = p_2 u_2 + \frac{1}{2} \omega u_2^2 + \omega E_2,$$

connecting the two uniform states between which it lies, and it is desired to find out whether it is thermodynamically possible, draw the lines M and N joining C and D, which are the points representing the states of the gas on the two sides of the discontinuity. If the line M lies above the line N (see diagram) so that p_m is greater than p_n then a condensation is possible. If the line M lies below the line N a rarefaction is possible. If the line M cuts the line N at any point between C and D, neither is possible.

The only special case of any importance is that of a perfect gas whose characteristic equations are

$$\frac{p}{\rho} = R\theta, \quad E - E_1 = \frac{R}{\gamma - 1} (\theta - \theta_1),$$

where γ is the ratio of the specific heats.

The general criterion is as above; but if we also assume constant conductivity κ and viscosity μ , the circumstances can be followed out in detail. In this case it may be shown that

$$X = -\frac{4\mu}{3\omega} \frac{du^*}{dx} \quad \text{and} \quad \omega \xi = -J\kappa \frac{d\theta}{dx}.$$

Substituting these values in equations (4) and (5),

$$p - \frac{4\mu}{3\omega} \frac{du}{dx} + \omega u = p_1 + \omega u_1,$$

$$\text{and} \quad \left(p - \frac{4\mu}{3\omega} \frac{du}{dx}\right) u + \omega \frac{u^2}{2} + \omega E - J\kappa \frac{d\theta}{dx} = p_1 u_1 + \omega \frac{u_1^2}{2} + \omega E_1.$$

* See Rayleigh's 'Theory of Sound,' vol. 2, p. 315.

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From these two equations, together with the equations

$$\frac{p}{\rho} = R\theta, \quad u\rho = \omega, \quad E - E_1 = \frac{R}{\gamma-1}(\theta - \theta_1),$$

the quantities p , ρ , E and θ may be eliminated.

The resulting equation is

$$\omega B u - \frac{1}{2} \omega u^2 + \frac{\omega}{\gamma-1} \left(\frac{4\mu}{3\omega} u \frac{du}{dx} + B u - u^2 \right) - \frac{\kappa J}{R} \left\{ \frac{4\mu}{3\omega} \frac{d}{du} \left(u \frac{du}{dx} \right) + (B - 2u) \frac{du}{dx} \right\} = \omega A,$$

where $\omega B = p_1 + \omega u_1$ and $\omega A = p_1 u_1 + \frac{1}{2} \omega u_1^2 + \omega E_1$.

It may be written in the simplified form

$$y \{ P dy/du - Qu + S \} + Mu^2 - Nu + A = 0, \quad (6)$$

$$\text{where } y = u \frac{du}{dx}, \quad P = \frac{4\mu\kappa J}{3\omega^2 R}, \quad Q = \frac{2\kappa J}{R\omega} + \frac{4\mu}{3\omega(\gamma-1)},$$

$$S = \frac{\kappa B J}{R\omega}, \quad M = \frac{\gamma+1}{2(\gamma-1)}, \quad N = \frac{B\gamma}{\gamma-1}.$$

If either $\kappa = 0$ or $\mu = 0$ (6) may be solved in the form

$$x = A \log(u_1 - u) + B \log(u - u_2),$$

where u_1 and u_2 are the roots of $Mu^2 - Nu + A = 0$.

If, however, neither μ nor κ vanish, (6) cannot be solved in finite terms, but if $u_1 - u_2$ be small compared with u_1 an approximate solution can be obtained.

If u_1 be the greater of the two roots of $Mu^2 - Nu + A = 0$, the solution is

$$x = \frac{Qu_1 - S}{M(u_1 - u_2)} \log \frac{u_1 - u}{u - u_2}. \quad (7)$$

By substituting for Q and S their values and remembering that $u_1 - u_2$ is small compared with u_1 , it may be shown that

$$Qu_1 - S = \frac{\kappa J}{R\omega} \left(1 - \frac{1}{\gamma} \right) + \frac{4\mu u_1}{3\omega(\gamma-1)},$$

which is positive. Hence (7) represents a condensation; for when u approaches u_1 , x approaches $-\infty$, and when u approaches u_2 , x approaches $+\infty$. From (7) it is possible to calculate approximately the thickness of the transition layer. It is evident that the distance between the planes where the velocities are u_1 and u_2 , is infinite; but to obtain some idea of the extent of the transition layer consider the thickness T of the layer in which

the velocity changes from $\frac{1}{T_0}u_1 + \frac{1}{T_0}u_2$ to $\frac{1}{T_0}u_1 + \frac{1}{T_0}u_2$. Substituting these values for u in (7)

$$T = \frac{Qu_1 - S}{M(u_1 - u_2)} \cdot 2 \log 9,$$

and inserting the values of γ , ρ , μ , and κ for air,

$$\gamma = 1.4, \quad \rho = 1.3 \times 10^{-3}, \quad \mu = 1.9 \times 10^{-4}, \quad \kappa = \frac{1.6 \mu R}{J(\gamma - 1)},^*$$

there is obtained $(Qu_1 - S)/M = 0.22$ and $T = (u_1 - u_2)^{-1}$ approximately.

In the case of waves of percussion it is known that the velocity differs appreciably from that of sound. In that case $u_1 - u_2$ would be considerable and its reciprocal would be small, so that the motion would closely approximate to an abrupt discontinuous one. In the case of ordinary sounds, however, the relative velocities of air in different parts of a wave are small, so that T would be large compared with a wave-length, and nothing in the nature of a sharp discontinuity would ever be established.

On the Radium Content of Basalt.

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received July 16, 1910.)

In a former paper† I gave measurements of the amount of radium in representative igneous rocks. In the reduction of these measurements a value of the equilibrium ratio between radium and uranium given by Rutherford and Boltwood was used, which has subsequently been corrected by those authors. My results were reprinted with the necessary amendment by Eve and McIntosh.‡

Subsequent to the publication of my first paper other experimenters have made similar measurements, with results in most cases substantially the same.§

Prof. J. Joly, however, has arrived at values considerably higher. His results are most conveniently referred to in his book "Radioactivity and

* O. E. Meyer, 'Kinetic Theory of Gases,' English edition, p. 292.

† 'Roy. Soc. Proc.,' A, vol. 77, p. 472.

‡ 'Phil. Mag.,' August, 1907, p. 231.

§ See Eve and McIntosh, *loc. cit.* Farr and Florence, 'Phil. Mag.,' November, 1908, p. 812. Schlundt and Moore, 'U.S. Geol. Survey Bull.,' vol. 395, p. 26. Fletcher, 'Phil. Mag.,' July, 1910, p. 36.

Geology" (Constable, 1909). The discrepancy is most marked in the case of basalts, for which he finds a value of 4.9×10^{-12} gramme radium per gramme of rock. My own results average about 0.6×10^{-12} , as also do those of the other experimenters. Prof. Joly does not find much difference between acid and basic rocks. Other experimenters have all found that acid rocks tend to be considerably richer.

I have made some additional measurements on basalts, in order, if possible, to clear up the cause of this discrepancy.

Special attention was paid to a point which had perhaps not been adequately considered in the earlier investigation. When the rock has been fused with sodium carbonate, and the product extracted with water, the aqueous solution obtained usually develops a precipitate on prolonged boiling. Formerly, this precipitate was allowed to remain in the alkaline liquid. In the present experiments it was filtered off and added to the acid liquid, in which it readily dissolved.

After extracting the sodium carbonate melt with water, the residue was formerly dissolved in hydrochloric acid, any silica which separated being allowed to remain in the liquid. In the present experiments this, too, was filtered off, and fused again with soda, the treatment being repeated if necessary, until everything had been got into solution. It was thought possible that the undissolved matter might be prejudicial to complete extraction of the emanation. But no such effect seems traceable in the results, and the trouble of preparing the solutions is greatly increased.

In other respects the method of experimenting was the same as before. The standardisations were carried out with several different analysed specimens of uranium ores, with fairly concordant results.

The mean values obtained from several readings with each rock were as follows:—

Description.	Radium per gramme, in grammes $\times 10^{-12}$.
Coarse-grained basalt. Hightown, near Belfast	0.16
Fine-grained basalt. Oelberg, Siebengebirge	0.33
Fine-grained basalt. Tobermory, Mull.....	0.35
Olivine basalt. Talisker Bay, Skye	0.57

These results are even lower than those obtained before for similar rocks. The actual material is different, except in the case of the last rock on the list, which gives about the same result as before.*

* This was the only one of the original basalts examined of which I had enough left for examination.

Thus the difference between my results and Prof. Joly's is somewhat emphasised. I should have regarded my results, if they stood alone, as sufficiently conclusive, though it is impossible to help feeling disconcerted by want of agreement with so distinguished an experimenter. It is perhaps possible, after all, that the difference is due to his having met with exceptional specimens.

Measurements of the Rate at which Helium is Produced in Thorianite and Pitchblende, with a Minimum Estimate of their Antiquity.

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received July 23, 1910.)

§ 1.—*Introductory.*

The method of deducing a minor limit to the age of minerals from an examination of their radioactive properties has, up to the present time, depended on a measurement of the amount of helium they now contain, and on an indirect calculation of the rate at which it is being produced by the radioactive matter within them.

There is not now much uncertainty about this calculation. Nevertheless, considering the fundamental importance of the question of geological time, it is not superfluous to determine in some favourable case by direct volume-measurement of the gas how much helium is produced per gramme of the mineral per annum, in order to see how long the quantity found in the natural mineral would take to accumulate, and to check the method of calculation to which we must still resort where the much more difficult direct method is impracticable.

A mineral suitable for such experiments must be obtainable by the kilogramme, and very radioactive, so as to give a measurable quantity of helium in a few months. The minerals selected have been thorianite (two varieties) and pitchblende—practically the only ones available.

Some account of preliminary work was given in a former paper.* Much more elaborate and satisfactory experiments have since been carried out. These will now be described.

* 'Roy. Soc. Proc.,' A, vol. 83, p. 98.

The great difficulty of the problem lies in the small quantities of gas which have to be dealt with. In this respect the conditions are far more onerous than in determinations of the helium production by radium; for a quantity of radium equivalent in activity to a ton of pitchblende or thorianite may be placed in a small vessel, and the helium developed in a given time extracted and measured. In the present investigation, the entire bulk of the original mineral has to be handled, and not merely the radium present in it. It is impracticable to work with more than a few kilogrammes in this way, thus the quantity of helium which can be obtained in, say, six months is small indeed.

Assuming the difficulty of the measurement of small volumes got over, there remains another not less serious. The helium initially present which has accumulated in geological epochs is perhaps 500 million times what the experimenter can grow under his observation. Thus, to make the experiment satisfactory, it is necessary to remove the helium so perfectly that not more than one part in 5,000 millions of the original stock remains.

This could never be done if the mineral were allowed to remain in its original solid condition. For solid minerals only yield their helium slowly and partially by heating.* It is essential, therefore, to get the mineral into solution, and to filter off any slight undissolved residue with the most scrupulous care. Prolonged boiling will then remove helium with the necessary completeness. It is important to use thick filter paper. Fine particles of undecomposed mineral may otherwise get through the pores. The importance of avoiding this will be understood when it is stated that the presence of 1/1000 of a milligramme of undecomposed thorianite was altogether inadmissible in my experiments. Much trouble was incurred through a failure to adopt this precaution in the earlier attempts.

The necessity for dissolving the mineral raises a theoretical question of some importance. Can we be really sure that this does not affect the rate of helium formation? I shall briefly discuss this question, chiefly for the convenience of those who approach the subject from a standpoint of general scientific interest, rather than as students of radioactivity.

Nearly all the evidence we have at the present time points to the conclusion that the rate of radioactive change is unalterable by anything that man can do. It is true that a few experimenters have thought that they could detect changes in radioactivity at high temperatures, but the experiments of Bronson,† which have been pushed further than any others, reveal no such effect up to

* Unless, indeed, very high temperatures are used, which would introduce many other difficulties.

† 'Roy. Soc. Proc.,' A, vol. 78, p. 494.

1600° C. The calorimetric experiments of Curie and Dewar showed no loss of heating effect in radium at liquid hydrogen temperatures. As the development of heat is quantitatively accounted for by the expulsion of α -particles (helium atoms) with a high velocity, it cannot be doubted that the helium emission is unaltered at these temperatures. More directly relevant are the experiments of Moore,* who found that radium emanation, dissolved in water, decayed at the same rate as when in the gaseous condition. As the decay is the direct consequence of the emission of α -particles, it is clear that here also helium formation is independent of circumstances, and, in particular, of whether the radioactive body is in solution or not.

Lastly the method is only applicable† if we assume that the rate of helium production has been the same throughout the whole geological period which it is sought to measure. What is there to be said in defence of this assumption? The critic will naturally object that the radioactive matter present is necessarily diminishing in quantity as it generates helium and other non-radioactive products to which it may give rise. There must, therefore, have been more of it at the beginning of the geological period considered than at the end, and consequently more rapid production of helium. The method as here applied is only valid if it can be shown that this diminution is unimportant in the period considered.

A simple argument goes far to establish this for thorianite. This mineral is a dense substance, consisting almost entirely of the parent radioactive bodies, uranium oxide and thorium oxide. We cannot suppose that there was ever much more of these bodies in the thorianite crystals than at present, for they do not contain much inactive matter of any kind, which can be assumed to represent the débris of the decayed radioactive bodies.

Apart from this simple argument, we have a good indirect estimate of the rate of decay of uranium,‡ which shows that it is unimportant in the periods here dealt with. The decay of thorium is almost certainly slower still.

The other chief line of objection which can be taken is that the rate of formation of helium depends on the physical condition of the radioactive matter. This objection has already been considered.

§ 2.—*Experimental.*

The thorianite used was dissolved in nitric acid, and most of the excess of acid driven off by evaporation. A slight insoluble residue then remained, consisting in the main of zircon which had been mixed with the thorianite.

* 'Roy. Soc. Proc.,' A, vol. 80, p. 597.

† At least, in the simple form with which alone this paper deals.

‡ Boltwood, 'Amer. Journ. Sci.,' June, 1908, vol. 25, p. 506.

This residue was filtered off and rejected. It would no doubt have been preferable to reject nothing, but much additional trouble would have been incurred in getting it into solution. The quantity of residue was insignificant and its activity much less than that of an equal weight of the original thorianite.

Two kinds of thorianite were used in the experiments, one the ordinary variety, the other that specially rich in uranium, from the Galle district. Besides the experiments on thorianite some were made on pitchblende. This mineral was treated with nitric acid, and the solution preserved separately. Pitchblende contains sulphides which were oxidised by the nitric acid. This led to precipitation of barium, radium, and lead as sulphates. The insoluble residue was boiled with large excess of sodium carbonate to expel sulphuric acid, and, after washing, again treated with nitric acid. After one or two repetitions of this process nothing but inactive sand remained. This was rejected. The solution obtained after the sodium carbonate treatment was, of course, kept separate from the original nitric acid solution. The helium obtained from these separate solutions was all measured together.

The various solutions were stored in vacuous round-bottomed flasks arranged as shown at *a* in fig. 1. A tall tube *b* serving as a reflux condenser was sealed to the neck of the flask, and was continued in a narrow tube *c*, with recurved end dipping down into a basin of mercury. The whole arrangement was fastened to a rod stand, and could be put away during the intervals allowed for the helium to be generated. When it was desired to collect the gas the liquid was boiled, taking care to raise the temperature slowly so that no violent bumping occurred. When vapour of appreciable pressure had formed over the liquid, boiling would proceed quite quietly, provided the solution was not too strong.

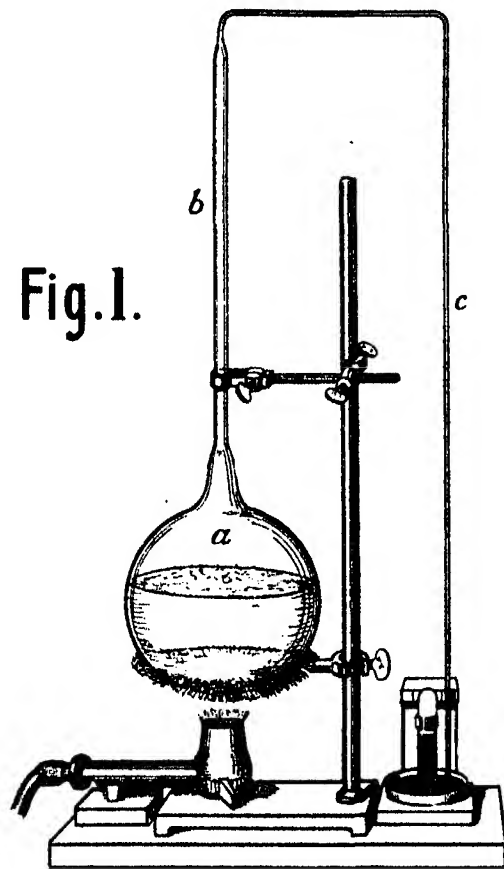
Boiling was continued by the application of a gentle heat, which did not raise more steam than could be condensed by the vertical tube, with simple air cooling.* The dissolved gases were expelled from the liquid, and accumulated in the upper part of the apparatus. They could be collected by increasing the heat under the flask, so as to wash them out with steam into a test tube inverted over the recurved end of the narrow delivery tube.

It was found that the nitric acid solutions invariably gave some nitric oxide, and a much smaller quantity of nitrogen. I have not paid special attention to the origin of this nitrogen, but it is certainly not atmospheric, as the absence of neon in the helium collected proves. It may be due to

* A fan was sometimes used to cool the tube, but without much advantage.

decomposition of nitric acid by radioactive bodies, but I have not tried whether it can be got from nitric acid only.

The gas collecting tube was half filled with oxygen, and some caustic potash floated on the surface of the mercury. Thus the nitric oxide was oxidised and absorbed. The excess of oxygen, carrying nitrogen and helium, was drawn into a gas burette and thence passed into a quartz tube

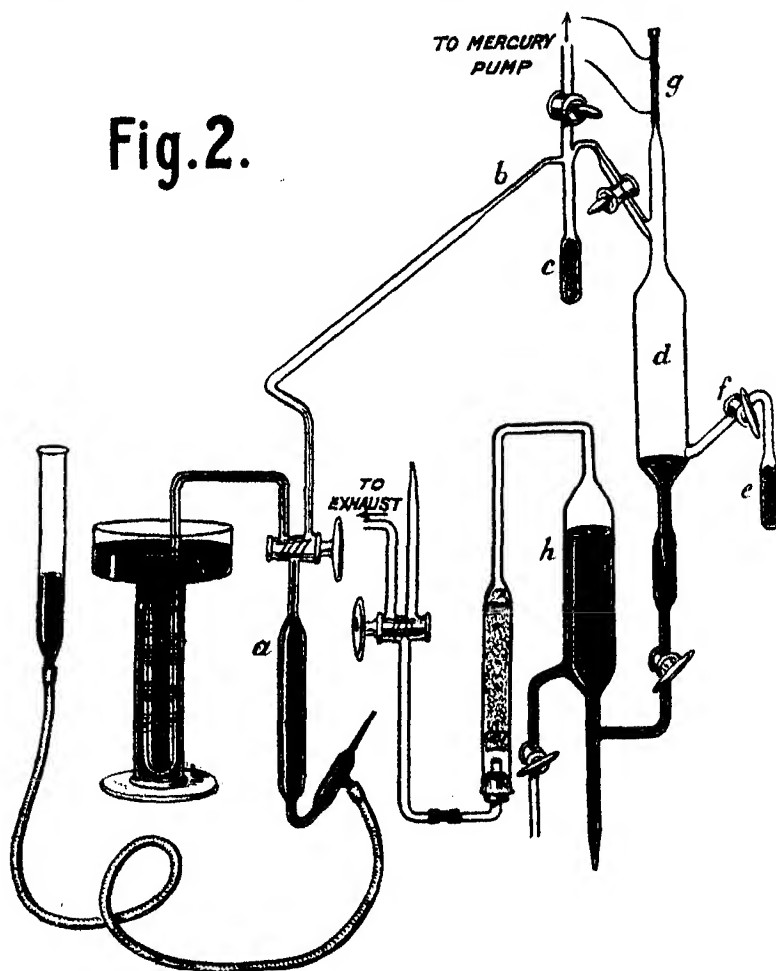


full of mercury with melted phosphorus at the top. The oxygen was burnt, and nitrogen, containing a small proportion of helium, remained. The flasks usually contained about 3 litres of solution, in which about 600 grammes of thorianite was dissolved. The nitrogen from each of them amounted to a fraction of a cubic centimetre, and served conveniently to carry the helium, in itself too little for pneumatic trough manipulation.

The final isolation of helium was effected by cooled charcoal. The apparatus used is shown in fig. 2. The gas is introduced into a gas pipette *a* with a two-

way stopcock, and thence into the exhausted apparatus. It is followed up with mercury as far as the point *b*. After standing for some time over the cooled charcoal in *c*, it is drawn into the large vessel *d*, where it comes into contact with more cooled charcoal in the annexe *e*; *d* is then heated to drive off any occluded gas, and allowed to cool. Ultimately *f* is closed, and *d* is filled with

Fig.2.



mercury so as to compress the residual helium into the capillary *g*. The arrangements for doing this are sufficiently obvious from the figure; *g* is a piece of very fine thermometer tubing 0.164 mm. diameter. The upper end, instead of being fused up, was closed by drawing a thread of melted sealing-wax into it. This gave an approximately plane end to the tube at right angles to its length, so that the volume of gas was calculable from the measured length it occupied, and the pressure. The latter was measured by taking the

difference of level between the mercury in *h* and in *g* by a cathetometer, and subtracting it from the barometric height.* The capillary depression in *g* (4.9 cm.) was allowed for. The actual pressure was about 20 cm. of mercury, and the length of tube occupied by the largest volume of helium generated under observation 7.3 mm. The length by the column of gas was measured by a microscope with ocular scale, or, when too long for that, by a mirror glass scale, estimating to 1/10 mm.

The apparatus lent itself very conveniently to spectroscopic observation of the gas, as a check on purity. Two strips of tinfoil on the capillary, at 2 or 3 cm. apart, were connected to an induction coil, and the pressure was reduced by lowering the mercury until the gas filled that part between the strips. When the helium was pure a bright yellow glow was observed, which became bluish with the slightest admixture of nitrogen. The spectroscope was, indeed, scarcely needed.

It was observed that if any trace of nitrogen remained it was rapidly removed by running the discharge for a short time, notwithstanding the absence of metallic electrodes, to which such actions are usually attributed. The volume of gas was, of course, diminished by this process; but, when once the nitrogen was gone, no amount of further sparking would diminish the volume of helium.

A correction to the measured volume is necessary, on account of the small quantity of helium which necessarily remains in the two charcoal vessels. This fraction was determined, once for all, by starting with pure helium introduced into *d* and measured. Connection was then made to *c* and *e*, both previously-exhausted and cooled. Cutting off these connections, the volume was measured again in *g*. It was found to be diminished by about 1/10 part.

The validity of the measurements depends, of course, on the assumption that no part of the very small volume of helium obtained is absorbed by the charcoal, under the conditions of the experiment. Although the absorption of helium at low pressures has been shown by Dewar and others to be very small, it was thought advisable to make direct tests. This was done as follows: A small quantity of helium was very largely diluted with oxygen, so as to form a standard mixture (of arbitrary composition). This was placed in a graduated tube, and 1 c.c. of it drawn into the apparatus. The helium contained measured 5.56×10^{-6} c.c., a volume comparable with the smallest obtained in the helium experiments. Seven cubic centimetres more of the mixture was then taken and most of the oxygen removed with phosphorus. The residue was added to the gas already in the apparatus, and the total helium (from 8 c.c. of mixture) measured as 4.73×10^{-6} c.c., 8.5 times that

* *h* was open to the atmosphere during the volume measurements.

from 1 c.c. This proved that no appreciable absorption took place. For, if there had been a slight absorption, it would have told much more on the small volume, and would have disturbed the ratio. Further evidence on this point will be given immediately.

§ 3.—*Results of Experiments.*

First Series.—Thorianite from Galle; the variety rich in uranium. Three flasks (numbered 4, 5, 6) set up, each containing 680 grammes in solution.

Experiment.	Volume of helium.
	c.c. $\times 10^{-6}$.
Initial blank test of all three flasks, D_3 invisible	<1.0
After 205 days' standing—	
Flask No. 4.....	15.5
Flask No. 4 + No. 5	34.9
Flask No. 4 + No. 5 + No. 6	45.9
Blank test of all three flasks, D_3 conspicuous	2.9
After standing 129 days more, all three flasks	24.3
Final blank test, D_3 invisible	<1.0

From these experiments—

Rate of production from all three flasks, per annum $\left\{ \begin{array}{l} 8.18 \times 10^{-8} \text{ c.c.} \\ 6.90 \times 10^{-8} \text{ c.c.} \end{array} \right.$

Mean $7.54 \times 10^{-8} \text{ c.c.}$

Rate of production per gramme of Galle thorianite,
per annum $3.7 \times 10^{-8} \text{ c.c.}$

Helium initially present, per gramme 9.3 c.c.

Time required to produce this $2.50 \times 10^8 \text{ years.}$

Second Series.—Ordinary thorianite containing 13.10 per cent. U_3O_8 , and 72.65 per cent. ThO_2 . Three flasks (numbered 1, 2, 3) set up, each containing 510 grammes.

Experiment.	Volume of helium.
	c.c. $\times 10^{-6}$.
Initial blank test of all three flasks, D_3 doubtful	<0.5
After standing 141 days*—	
Flask No. 1.....	5.0
Flask No. 1 + No. 2	11.3
Flask No. 1 + No. 2 + No. 3	16.5
Final blank test of all three flasks	<0.5

* As a matter of fact, the flasks were not all boiled out at quite the same time on this occasion. The numbers given are slightly corrected to compensate for this, so that the results can be studied more easily.

From these experiments—

Rate of production from all three flasks per annum	4.27×10^{-5} c.c.
Rate of production per gramme of ordinary thorianite	2.79×10^{-8} c.c.
Helium initially present, per gramme	7.8 c.c.
Time required to produce this	2.8×10^8 years.

Pitchblende, from Joachimsthal, 353 grammes. Dissolved (see above, p. 382) in two separate flasks, which were always boiled at the same time, and the gases treated together.

Experiment.	Volume of helium.
	c.c. $\times 10^{-6}$.
Blank test, D_2 invisible	< 0.5
After 61 days (not a good experiment).....	2.0
After 294 days (good experiment).....	9.0

The last experiment is the only one on which stress can be laid. It gives

Helium per gramme pitchblende, per annum..... 3.16×10^{-8} .

The pitchblende experiments were not carried so far as those on thorianite, on account of the much greater difficulties of preparing the solution. The best experiment, however, was a very satisfactory one.

The helium measured may be exhibited graphically as a function of the

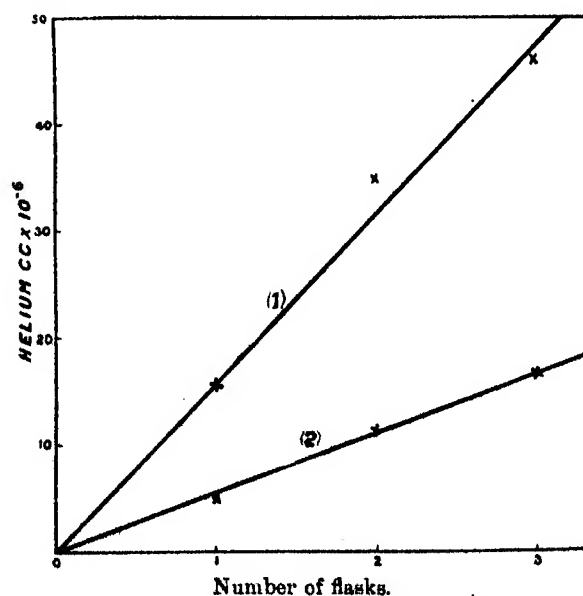


FIG. 3.—(1) Galle thorianite. (2) Ordinary thorianite.

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number of flasks emptied, in those cases where the contribution of each was added successively, and shows fair proportionality (fig. 3). This is additional evidence that no appreciable helium was lost in the charcoal, otherwise the first flask would have apparently yielded less than its due contribution.

§ 4.—*Discussion of Results.*

It now remains to compare the rate of formation of helium observed with that calculated theoretically. For the calculation I refer to 'Roy. Soc. Proc.' A, vol. 81, p. 276, and vol. 83, p. 97.

Mineral.	U ₃ O ₈ . Per cent.	ThO ₂ . Per cent.	Helium production per gramme per annum. C.c. × 10 ⁻³ .	
			Observed.	Calculated.
Thorianite. Galle district ...	24·50	65·44	3·70	3·46
Ordinary thorianite	13·10	72·65	2·79	2·55
Pitchblende	87·6	None	3·16	3·44

The calculation is clearly justified by the direct observations, and can in future be employed with confidence in its substantial correctness.

The present experiments leave, I think, no doubt whatever that some specimens of thorianite are as much as 280 million years old. I will take this opportunity of summarising the data in my previous papers* with regard to the duration of geological time, as deduced by the indirect method. With the verification of this method now presented, I feel justified in stating them numerically without the qualifications before insisted on.

Mineral.	Geological horizon.	Minimum age.
		Years.
Sphaerosiderite from Rhine provinces	Oligocene	8,400,000
Hæmatite, Co. Antrim	Eocene	81,000,000
Hæmatite, Forest of Dean	Carboniferous limestone ...	150,000,000
Sphene, Renfrew Co., Ontario	Archæan	710,000,000

These are minimum values, because helium leaks out from the mineral, to what extent it is impossible to say.

Summary.—The rate at which helium has been and is being produced in thorianite has been measured directly with reasonable accuracy, and is found to be in agreement with the rate calculated indirectly. The helium now found in one sample examined would take 280 million years to accumulate. Similar measurements have been made with pitchblende.

* 'Roy. Soc. Proc.' A, vol. 81, p. 272; vol. 83, p. 96; vol. 83, p. 298.

*Observations on the Anomalous Behaviour of Delicate Balances,
and an Account of Devices for Increasing Accuracy in
Weighings.*

By J. J. MANLEY, Hon. M.A. Oxon., Daubeny Curator, Magdalen College,
Oxford.

(Communicated by Prof. E. B. Elliott, F.R.S. Received June 21,—
Read November 10, 1910.)

(Abstract.)

Many observers have drawn attention to the small irregularities that are frequently exhibited by delicate balances. The consequent inconveniences appear to have been felt chiefly by those who have been engaged in atomic weight determinations, the measurements of the mean density of the earth, the standardisation of weights, and work of a like nature. Of those who have thus been hampered during their researches we may mention the names of such well-known investigators as Miller, Thorpe, Poynting and Phillips, and Dixon and Edgar.

In this paper an account is given of experimental work that was carried out with the object of elucidating the causes of the variations in the resting-point of a balance. Through the kindness of the agents of various balance makers, the author was enabled to experiment with a number of new instruments of high grade and of different types.

It appeared probable that the possible causes of the fluctuations in the resting-point were due to

- (1) Side-slipping of the central knife-edge upon its supporting plane.
- (2) Differential and continued flexure of the beam after loading.
- (3) Lateral displacement of one or more knife-edges.
- (4) Small variations in the temperature of the two arms of the beam.

Each of the four possibilities is investigated in detail both experimentally and theoretically. It is shown that the anomalous behaviour of a balance is due almost, if not quite entirely, to causes (3) and (4), and that causes (1) and (2) are, for all practical purposes, inoperative.

Experiments were conducted by means of a differential bolometer placed within the ordinary balance case. They revealed the existence of slight but rapid and almost continuous fluctuations in the temperature of the air immediately surrounding the beam. These fluctuations cannot be detected by even very delicate mercury-in-glass thermometers; for such thermometers

are too sluggish to respond to them, and record a mean temperature only.

When the pans are being loaded or unloaded, the variations in the temperature of the two arms are, as we should naturally expect, largely increased; and if a weighing is effected immediately after the necessary weights have been placed upon the pan, there is considerable uncertainty as to the true weight of the object under measurement. For accurate weighing, the final observations should not be taken before some 10 to 15 minutes have elapsed after loading.

Other experiments appear to prove that the knife-edge blocks require, not infrequently, some little time to take up a normal position for a given load. Balances which have their knife-edges attached to the beam in a certain manner often show this kind of defect somewhat markedly.

When it is required to determine the mass of a body with the highest degree of accuracy, it is necessary to fatigue the balance-beam by allowing it to swing freely for some time after the object and weights have been placed upon the pans. The time required to reduce a balance to a normal condition in this way, depends both upon the instrument and upon its load. It was found that some balances may be completely fatigued within a few minutes, while others require a more prolonged period. So far as I am able to judge from my own observations, it appears that from 10 to 20 minutes are generally sufficient for the purpose.

Any abnormal temperature effects that may be produced whilst the pans are being loaded will also die away during the time required for fatiguing the beam.

It was also found that the resting-point changes in a perfectly regular manner with an increase or decrease in the temperature of the beam. The magnitude of the change depends upon the type of the balance and its load; also, two different balances of the same type and by one maker may have totally different temperature coefficients.

The temperature coefficients appear to be best represented by an equation of the form

$$M = M_1(1 \pm \alpha t \pm \beta t^2),$$

in which M and M_1 are respectively the true and apparent masses, and α and β are factors which must be determined for different loads and for each balance.

It is also shown that a distinct advantage is gained and some marked irregularities avoided, by surrounding the beam with an extra inner case consisting of metal, wood, and plate glass. By the introduction of this device, the beam is permanently screened from heat radiations and

convection currents, even when the ordinary shutter of the balance case is lifted.

An additional advantage is gained by placing a differential bolometer within the inner or beam case; for we are then enabled to ascertain, at any time, whether the temperature of the two arms is uniform or not.

Some few of the numerous results are represented graphically rather than in tabular form. In this way the facts to which it is desired to draw attention are brought out more clearly and prominently.

The dispositions and forms of the apparatus used are shown in diagrams; the efficiencies of the various forms of knife-edges employed in balances are also discussed.

The Damping of Sound by Frothy Liquids.

By A. MALLOCK, F.R.S.

(Received May 26,—Read June 23, 1910.)

The fact that a tumbler containing a frothy liquid gives a dull sound when struck is familiar to every one, but I cannot find that any explanation of the rapid damping of the vibrations, which is indicated by the character of the sound, has been published.

The converse case, namely, that of waves propagated through a gas in which small solid or liquid spheres are disseminated, has received considerable attention, and the results deduced, which agree with observation, are to the effect that although the presence of small obstacles does cause some damping, it is very small in amount.

I think there can be little doubt that the excessive damping in the case where the obstacles are gaseous, and the intervening spaces filled with liquid, is due to the augmentation of the distortion of the latter caused by the variation of pressure acting mainly on the volume of the gas.

When no gas bubbles are present in a liquid transmitting vibrations, distortion accompanies changes of pressure, but the rate at which shear takes place is of the order amplitude \div wave-length, and in liquids the velocity of transmission is large, and also the wave-length in cases where the frequency is that of an audible note.

On the other hand, if bubbles of gas are present the variation of pressure acts almost entirely on the volume of the gas, and scarcely at all on the relatively incompressible liquid. Thus, if S, fig. 1, be part of the surface of

a bubble at the mean pressure, which under the variation of pressure changes its radius from OS to OS' and OS'' , the liquid in the element whose mean position is AB changes from $A'B'$ to $A''B''$, and the difference of the lengths $A'B'$ and $A''B''$ is a measure of the distortion caused by the

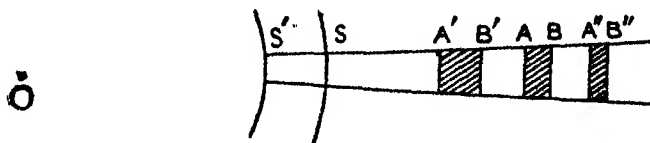


FIG. 1.

variation of pressure. For a given variation of volume the distortion increases as the radius of the bubble diminishes. It must be assumed that the change is never large enough to make the pressure or radius of the bubble vary much from their mean values.

The nature of the stress to which a non-viscous liquid in a vibrating cylindrical vessel is exposed depends on the ratio of the wave-length in the liquid to the transverse dimensions of the vessel. If this ratio is large the stress in the liquid is one of shear only, the compression and dilation at all points being neutralised by the symmetry of the motions of the vibrating walls. If, however, the velocity of propagation is so slow that the diameter of the vessel is a considerable fraction of a wave-length, there will be changes of pressure in the liquid as well as distortion, and it is only variation of pressure which will make the damping action of gas bubbles effective in the way supposed.

It may be remarked that the velocity of transmission of a wave in mixed fluid, such as a liquid containing bubbles, is the same as it would be in a homogeneous fluid of the same density and mean elasticity.

Thus, ρ and E being the mean density and elasticity of the mixture, if the volume, density, and elasticity of the liquid and gas are respectively v_1 , ρ_1 , E_1 , and v_2 , ρ_2 , E_2 , and if $v_1 = lv_2$, $\rho_1 = m\rho_2$, $E_1 = nE_2$, the velocity of transmission is $\sqrt{E/\rho}$, and $dv_1/v_1 = dp/E_1$, $dv_2/v_2 = dp/E_2$, if dp is the variation of stress. Hence, in terms of E_2 ,

$$E = E_2 \frac{n(l+1)}{l+n}.$$

Also

$$\rho = \frac{\rho_1 v_1 + \rho_2 v_2}{v_1 + v_2} = \rho_2 \frac{ml+1}{l+1};$$

so that

$$\sqrt{E/\rho} = \sqrt{\frac{E_2}{\rho_2}} \frac{(l+1)\sqrt{n}}{\sqrt{(l+n)(ml+1)}}.$$

Thus, if the gas is air,

$$\frac{\text{Velocity of wave propagation in mixture}}{\text{Velocity of sound in air}} = \frac{(l+1)\sqrt{n}}{\sqrt{(l+n)(ml+1)}}.$$

This has a minimum when $l = (n-2)/(m-1)(n-1)$, which makes l very nearly unity in the case of a water and air mixture. The form of the velocity curve is shown in fig. 2, in which the abscissa is the value of l .

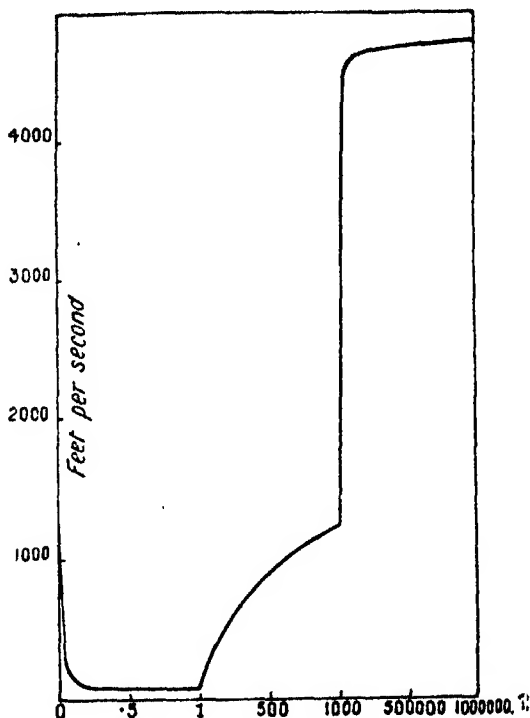


FIG. 2.

It will be seen that a very small quantity of liquid, when distributed as in froth, lowers the velocity of transmission enormously, and that the velocity again rises to that of sound in air when the volume of air is about 1/800 of the whole. When l is less than 2, the mixture begins to take the nature of a froth. The velocity rises very gradually as the quantity of air diminishes, reaching, of course, ultimately (and sensibly when $l = 1$ million) the velocity of propagation in water.

As before mentioned, it is only alterations in the volume of the mixture which produce excessive dissipation of the energy of the vibrations, and the character of the action may be examined by computing the dissipation for the case of a spherical bubble of gas surrounded by a sphere of viscous, but

incompressible fluid, subjected over its outer surface to a harmonic radial displacement of given amplitude.

Let r_1 and r_2 be the radii of the sphere and enclosed bubble respectively, and let a_1 be the amplitude of the vibration at r_1 ; also let T be the period of the vibration and $2\pi/T = p$.

Since the liquid is incompressible, the amplitude at r is $a = a_1 r_1^2/r^2$, and if e_0 is the thickness of a spherical shell of mean radius r when the liquid is at rest, and e its thickness at time t when vibration is going on, $(e_0 - e)/e = 2a \sin pt$, and this quantity differentiated with respect to time is proportional to the rate of shear.

The rate of shear is therefore proportional to $2ap \cos pt/r$, and for a shell of thickness dr , the speed with which the spherical faces approach or recede from one another is $2ap \cos pt dr/r$, and the force required (over the whole shell) to cause shear at this rate is proportional to $4\pi\mu r^2 2ap \cos pt/r$.

The work done (as far as it depends on viscosity) in time dt is proportional to $4\pi\mu r^2 (2ap \cos pt/r)^2 dr dt$, and substituting $a_1 r_1^2/r^2$ for a , and taking account of the tangential, as well as the radial, variations in the dimensions of the shell, it will be found* that the dissipation in dt , i.e. the work done in overcoming the viscous reaction, is $36\pi\mu p^2 a_1^2 \cos^2 pt \cdot r_1^4/r^4 \cdot dt dr$. Integrating, therefore, from $r = r_1$ to $r = r_2$, and from $t = T$ to $t = 0$, the dissipation throughout the whole sphere during one complete period is

$$12\pi\mu p^2 a_1^2 r_1 \left(\frac{r_1^3 - r_2^3}{r_2^3} \right).$$

The whole energy of vibration in the liquid and bubble is

$$\int_{r_2}^{r_1} 4\pi\rho r^2 \left(p a_1 \frac{r_1^2}{r^2} \right)^2 = 4\pi\rho a_1^2 p^2 r_1^3 \left(\frac{r_1^3 - r_2^3}{r_2^3} \right).$$

Hence the ratio of the work dissipated in time T to the whole energy in the liquid is $3 \frac{\mu}{\rho} T \frac{r_1^2 + r_1 r_2 + r_2^2}{r_1^2 r_2^2}$, or (since $\mu/\rho = \nu$ and $r_1^3 - r_2^3 = l r_2^3$; also, for brevity, putting L for $(l+1)^{\frac{1}{2}}$), we have

$$\frac{\text{Work dissipated per vibration}}{\text{Total energy in liquid}} = \frac{3\nu T}{2r_2^2} \frac{L^2 + L + 1}{L^2}.$$

Thus the efficiency of the bubbles in damping vibrations increases rapidly, both as their diameter and the distance between them (measured by r_1) diminish. The damping per vibration is proportional to the period T , but for a constant time is independent of T , the reduction for all periods being in the ratio of $1/e$ when $t = r_2^2 L_2/\nu (L^2 + L + 1)$. The increased damping

* See Lamb's 'Hydrodynamics,' § 317.

effect when the bubbles are small is borne out by observation, but it is difficult to make quantitative experiments in these cases.

When the proportion of air to water is large the mixture becomes a froth that is a mass of polygonal bubbles separated by thin films of liquid. The problem of evaluating the viscous reaction in such a mixture is one I have not attempted to solve. Experiment, however, shows that froth is a most efficient agent in damping vibrations.

This may be shown in a simple and striking way as follows:—Having prepared a sufficient quantity of fine grained froth in a flat dish with soap and water, take a wine glass or tumbler which gives a clear musical note when struck. Dip the mouth of the glass into the froth for about a quarter of an inch and withdraw it. A thin ring of froth will be left round the edge, weighing, perhaps, 1 or 2 grains. Small as this quantity of froth is it will be found sufficient to damp the vibration so rapidly as to almost deprive the sound of any musical character.

On the Determination of the Tension of a recently formed Water-Surface.

By N. BOHR, Copenhagen.

(Communicated by Lord Rayleigh, O.M., F.R.S. Received August 22,—
Read November 10, 1910.)

As an addition to my paper, published in the 'Philosophical Transactions,'* on the determination of the surface-tension of water, I desire to set forth the following remarks concerning the problem of the value of the tension of a recently formed water-surface, and the circumstances which are of importance for the determination of this tension.

Prof. P. Lenard has, in a paper lately published,† determined the surface-tension of a recently formed water-surface by means of the vibration of falling drops, and has for this tension found values which are considerably greater than those found by other methods. From this, as well as from the results of experiments published in a former paper,‡ he concludes that a recently formed water-surface has a very great tension, which, however,

* 'Phil. Trans.,' A, 1909, vol. 209, p. 281.

† 'Sitzungsber. d. Heidelberger Akad. d. Wiss.,' Math.-nat. Kl. Jahrg. 1910, Abh. 18.

‡ 'Ann. d. Phys. u. Chem.,' 1887, vol. 30, p. 209.

in the course of a very short time (fraction of a second) decreases considerably. He remarks that this result is in agreement with experiments published in my paper mentioned above. I shall, however, in the following try to explain the reasons why I cannot agree in these conclusions.

The determination of the surface-tension published in my paper cited above was carried out by the method of jet-vibrations, the theoretical foundation of which method, as well as of the method used by Prof. Lenard, is due to Lord Rayleigh.*

As to the closer investigation of the vibration of the jets, especially with regard to the satisfaction of the suppositions made in the theoretical treatment of the phenomenon, a great number of vibrations, commencing just at the orifice and in the most stable jets extending to a distance of more than 45 cm. from this (the velocity of the jets was about 425 cm./sec.), were examined by my experiments. These measurements showed that the wave-length was not the same everywhere, but that, advancing from the orifice, it increased in the beginning rather rapidly and thereupon more slowly until finally from a distance of about 25 cm. from the orifice and as far as the stability of the jet allowed the measurements, the wave-length became practically perfectly constant. (See the tables, *loc. cit.*, pp. 310—312.)

This result consequently showed the existence of certain irregularities of the phenomenon, which arise in the formation of the jet, and which are rapidly (in about 0.06 sec.) extinguished (*loc. cit.*, p. 309).

These irregularities might partly be thought to originate from possible variations of the value of the surface-tension in the time immediately after the formation of the surface, partly from irregularities of a more mechanical (hydrodynamical) character (*loc. cit.*, p. 299). Since the last-mentioned irregularities, as explained in my former paper, must decrease rapidly on removal from the issue of the jet, the result of the experiments showed that the surface-tension, in every case from about 0.06 second after formation of the surface, and as long as it was possible to investigate the tension by the used method, was sensibly constant.† This constant value was considered as

* 'Roy. Soc. Proc.' 1879, vol. 39, p. 71.

† Prof. Lenard remarks in his last paper (*loc. cit.*, p. 4) that the mechanical irregularities certainly must decrease, but cannot, even far from the orifice, completely disappear, on account of the resistance of the air against the movement of the jet. As, however, the effect of the air resistance removing from the orifice very rapidly will become constant, we see that an influence of this resistance on the phenomenon will not affect the above conclusion of the constancy of the surface-tension, but it can only cause an alteration of the value found for this constant tension. As to the question of the magnitude of the influence of the air resistance, I mention here an unpublished experiment made during my first investigation. Around the jet, at a distance of about 10 cm. from the orifice, was placed a large and carefully worked iris diaphragm, so

the sought value for the surface-tension, and it was in every case the only one which could be compared with values found by other methods, in which the investigated surfaces always have been much older than 0.06 second.

Concerning the question of a possible variation of the surface-tension during the time from the formation of the surface until some 0.06 second later, it seems to me that my experiments do not give any reason to conclude an existence of such a variation, there being, as we shall see, no objection in explaining the found variation in the wave-length by help of the velocity-differences between concentric parts of the jet produced by friction during its formation, by which the central parts receive a greater velocity than the parts nearer the surface. These velocity-differences decrease, removing from the issue, on account of the viscosity in the jet; the mean velocity of the jet keeping constant, this effects that the velocity of the outer parts increases at the same time as the velocity of the central parts decreases. That the wave-lengths are shorter close to the orifice than at a greater distance from this has always seemed to me to be a natural consequence of the velocity of the surface (the outer parts) here being smaller and the waves in question being surface-waves (the velocity of the vibrating liquid-particles is becoming smaller removing from the surface, and is vanishing in the axis of the jet). In his above-cited paper (*loc. cit.*, p. 4), Prof. Lenard, however, is of the opinion that the inner mixture—produced during the vibrating motion, on account of the mutual displacing of the concentric parts of the jet—will effect an apparent increase of the mass, and a thereby resulting prolongation of the time of vibration and increase of the wave-lengths.

For the closer examination of this question, I have therefore made the following direct calculation of the wave-lengths, under the assumption that the different concentric parts of the jet are moving with different velocities.

that the jet just passed through the centre of the diaphragm. This was at first open, so that a free space of 5 cm. (the opening of the diaphragm was 10 cm.) surrounded the jet. Thereupon the diaphragm was closed, so that the free space between the jet and the diaphragm was not more than some 0.2 mm., and at the same time a wave-summit of the jet at a distance of 30 cm. from the orifice was fixed in a telescope by help of reflection in the surface of the jet (*loc. cit.*, p. 305). It was then observed that the mentioned summit during the closing of the diaphragm was displaced only very little (less than 0.1 mm.). This simple experiment was repeated several times with exactly the same result. As such a closing of the diaphragm must increase the resistance of the air to a very considerable degree, completely stopping the mass of air set in motion by the jet (the jet produces a sensible blast), the experiment, in my opinion, shows very distinctly that the air resistance cannot have any appreciable influence on the results. As will be shown in the following, an air resistance would besides introduce a correction of the value of the surface-tension, the sign of which would be opposite to that supposed by Prof. Lenard.

The general equations of motion of an incompressible non-viscous fluid unaffected by extraneous forces, are

$$\rho \frac{Du}{Dt} = -\frac{\partial p}{\partial x}, \quad \rho \frac{Dv}{Dt} = -\frac{\partial p}{\partial y}, \quad \rho \frac{Dw}{Dt} = -\frac{\partial p}{\partial z}, \quad (1)$$

$$\text{and} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad (2)$$

in which u, v, w are the components of the velocity, p the pressure, ρ the density, and

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z}.$$

In the problem in question the motion will be steady. Putting $w = W + \omega$, and supposing that u, v , and ω are so small that products of them, and quantities of the same order of magnitude, can be neglected in the calculations, we get from the equations (1)

$$\rho W \frac{\partial u}{\partial z} = -\frac{\partial p}{\partial x}, \quad \rho W \frac{\partial v}{\partial z} = -\frac{\partial p}{\partial y}, \quad \rho \left(u \frac{\partial W}{\partial x} + v \frac{\partial W}{\partial y} + w \frac{\partial w}{\partial z} \right) = -\frac{\partial p}{\partial z}. \quad (3)$$

Introducing polar co-ordinates r and \mathfrak{S} ($x = r \cos \mathfrak{S}$, $y = r \sin \mathfrak{S}$), and the radial and tangential velocity α and β , we get by help of the relations

$$u = \alpha \cos \mathfrak{S} - \beta \sin \mathfrak{S}, \quad v = \alpha \sin \mathfrak{S} + \beta \cos \mathfrak{S},$$

from (3), assuming W to be a function of r only.

$$\rho W \frac{\partial \alpha}{\partial z} = -\frac{\partial p}{\partial r}, \quad \rho W \frac{\partial \beta}{\partial z} = -\frac{1}{r} \frac{\partial p}{\partial \mathfrak{S}}, \quad \rho \left(\alpha \frac{dW}{dr} + W \frac{\partial \omega}{\partial z} \right) = -\frac{\partial p}{\partial z}, \quad (4)$$

$$\text{and from (2)} \quad \frac{\partial \alpha}{\partial r} + \frac{\alpha}{r} + \frac{1}{r} \frac{\partial \beta}{\partial \mathfrak{S}} + \frac{\partial \omega}{\partial z} = 0. \quad (5)$$

Now, supposing that p, α, β , and ω have the form $f(r) e^{i n \mathfrak{S} + i k z}$, we get from (4) and (5)

$$\frac{\partial^2 p}{\partial r^2} + \frac{\partial p}{\partial r} \left(\frac{1}{r} - \frac{2}{W} \frac{dW}{dr} \right) - p \left(\frac{n^2}{r^2} + k^2 \right) = 0. \quad (6)$$

In the case W is constant, the solution of (6), subject to the condition to be imposed when $r = 0$, is

$$p_0 = A J_n(i k r) e^{i n \mathfrak{S} + i k z}, \quad (7)$$

in which J_n is the symbol of the Bessel's function of n th order.

$$\text{Putting} \quad p = p_0 e^{\int \psi(r) dr}, \quad (8)$$

we get from (6)

$$\frac{d\psi}{dr} + \psi^2 + \psi \left(\frac{1}{r} + \frac{2}{p_0} \frac{\partial p_0}{\partial r} - \frac{2}{W} \frac{dW}{dr} \right) - \frac{2}{p_0 W} \frac{\partial p_0}{\partial r} \frac{dW}{dr} = 0. \quad (9)$$

We will now suppose that $W = c + \sigma$, in which the constant c is the mean velocity of the jet, and σ a quantity small compared with c . In this case ψ is small, and neglecting terms of the same order of magnitude as $(\sigma/c)^2$, we get from (9)

$$\frac{d\psi}{dr} + \psi \left(\frac{1}{r} + \frac{2}{p_0} \frac{\partial p_0}{\partial r} \right) - \frac{2}{cp_0} \frac{\partial p_0}{\partial r} \frac{d\sigma}{dr} = 0. \quad (10)$$

In the experiments the numerical value of ikr will be a very small quantity—the wave-length large in comparison to the diameter of the jet—in order not to complicate the formulæ, we will therefore in the calculation of ψ only use the first term of the expression for $J_n(ikr)$. This gives $\frac{1}{p_0} \frac{\partial p_0}{\partial r} = \frac{n}{r}$, and the solution of (8) becomes

$$\psi = \frac{2n}{c} r^{-(2n+1)} \left\{ \int_0^r \frac{d\sigma}{dr} r^{2n} dr + \epsilon \right\}.$$

The motion being finite for $r = 0$, we have $\epsilon = 0$.

Integrating by part we get

$$\psi = \frac{2n}{cr} \sigma - \frac{4n^2}{cr^{2n+1}} \int_0^r \sigma r^{2n-1} dr. \quad (11)$$

Let us suppose that the equation of the surface is

$$r - a = \zeta = R e^{ins + ikz}.$$

The general surface condition gives

$$\frac{1}{i\eta} (r - a - \zeta) = \left(\alpha \frac{\partial}{\partial r} + \frac{\beta}{r} \frac{\partial}{\partial s} + w \frac{\partial}{\partial z} \right) (r - a - \zeta) = 0,$$

whence we get, neglecting quantities of the same order of magnitude, as by the equations (3)

$$\alpha - W \frac{\partial \zeta}{\partial z} = 0, \quad \zeta = -\frac{i}{Wk} \alpha.$$

In the same manner we get further, if the principal radii of curvature are R_1 and R_2 ,

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{a} - \frac{\zeta}{a^2} - \frac{1}{a^2} \frac{\partial^2 \zeta}{\partial s^2} - \frac{\partial^2 \zeta}{\partial z^2} = \frac{1}{a} - \alpha \frac{i(n^2 - 1 + k^2 a^2)}{a^2 W k}.$$

Calling the surface-tension T , the dynamical surface-condition will be

$$T \left(\frac{1}{R_1} + \frac{1}{R_2} \right) - p = \text{const.}$$

From this we get, with the same approximation as before and using (4)

$$\left[T \frac{(n^2 - 1 - k^2 a^2)}{\rho a^2 k^2 W^2} \frac{\partial p}{\partial r} - p \right]_{r=a} = 0. \quad (12)$$

From (12) we get, using (7) and (8),

$$k^2 = T \frac{iak J'_n(ik a)}{\rho a^2 J_n(ik a)} (n^2 - 1 + a^2 k^2) \left\{ \frac{1}{W^2} \left(1 + \psi \frac{p_0}{\partial p_0 / \partial r} \right) \right\}_{r=a}. \quad (13)$$

From (13) we get, by help of (11) and with the same approximation as used in the calculation of ψ ,

$$k = T \frac{iakJ'_n(iak)}{\rho c^2 a^3 J_n(iak)} (n^2 - 1 + a^2 k^2) \left[1 - \frac{4n}{ca^{2n}} \int_0^a \sigma r^{2n-1} dr \right]. \quad (14)$$

This equation is, except the last term, the solution given by Lord Rayleigh. We therefore see that the effect of the velocity-differences between concentric parts of the jet consists in an exchange in the formula for the wave-length λ ($\lambda = 2\pi/k$), of the mean velocity of the jet c by an "effective mean velocity,"

$$c' = c + \frac{2n}{a^{2n}} \int_0^a \sigma r^{2n-1} dr. \quad (15)$$

We see from (15) that the greater n is, the nearer the effective mean velocity will be to the velocity of the surface, which is explained by the fact that the greater n (the number of waves on the circumference of a section of the jet) is, the more rapidly the velocity of the vibrating liquid particles will decrease, moving from the surface towards the axis of the jet.

It can now be shown that c' will be smaller than c , if the velocity of the jet—which will be the case in the experiments—is greatest in the middle and continually decreases approaching the surface; c being the mean velocity of the jet, we have $\int_0^a \sigma r dr = 0$, and in the case in question further $\int_0^r \sigma r dr > 0$, where $a > r > 0$. From this we get for $n \geq 2$ (in the experiments $n = 2$).

$$c' - c = \frac{2n}{a^{2n}} \int_0^a \sigma r^{2n-1} dr = -\frac{2n(2n-2)}{a^{2n}} \int_0^a \left[\int_0^r \sigma r dr \right] r^{2n-3} dr < 0. \quad (16)$$

After having seen that the velocity-differences in question will produce a variation of the wave-length in the same direction as found by the experiment, we shall further see how the decrement of the variation of the wave-length can also be approximately explained by the manner in which the velocity-differences will decrease. In order to show this, we shall use the four experiments quoted in the table, *loc. cit.*, p. 310. In the table below is quoted the mean radius of the jet a , the velocity v (calculated from the mean radius and the discharge), and under the indication D_2/D_1 , the difference between the wave-length, measured between the wave-summits IV and V, and the constant value to which the wave-lengths were tending, divided by the corresponding difference between the wave-length, measured between the summits II and III, and the mentioned constant value (in these differences are introduced the small corrections for the curvature of the jet and for the wave-amplitudes mentioned in the table, *loc. cit.*, p. 311); under the

indication l is quoted the difference between the mean value of the readings of the summits IV and V and the mean values of the readings II and III. Further, under the indication α is quoted the ratio between the variations of the wave-length in two places corresponding to a time-interval of $1/100$ sec. (calculated on the assumption that the variations decrease after an exponential law). Under the indication α' is finally quoted the ratio between the velocity differences in the jet in two places corresponding to a time-interval of $1/100$ sec., calculated from the theoretical formula, *loc. cit.*, p. 298, l. 2. f. b.

	I.	II.	III.	IV.
a	0·06755	0·07554	0·07595	0·08010
c	426	428	426	429
$\frac{D_2}{D_1}$	0·54	0·53	0·53	0·50
l	4·30	5·16	5·16	5·59
$\alpha = \left(\frac{D_2}{D_1} \right)^{\frac{r}{100l}}$	0·54	0·59	0·59	0·59
$\alpha' = e^{-\frac{\mu}{\rho} \left(\frac{\pi^2 2167}{\alpha} \right)^2 \frac{1}{100}}$	0·67	0·72	0·73	0·75

As will be seen, the calculated and the found values for the decrement of the variation of the wave-lengths agree with regard to the order of magnitude, and more was not to be expected from such an approximate calculation. It is thus not justified to expect that the distribution of the velocity in jet-sections so close to the orifice could be completely expressed by the first term in the general formula on p. 298.

After having now seen that my experiments do not give any reasons for the conclusion of the existence of a variation in the surface-tension during the first time after the formation of the surface, we shall proceed to mention the values for the surface-tension of a recently formed water-surface found by Prof. Lenard by his investigations of the vibrations of falling drops.

The surfaces there investigated must, in my opinion, be considered as much older than the surfaces investigated by my experiments, on account of the length of the time used for the formation of the drops. Prof. Lenard remarks in his last paper [*loc. cit.*, p. 11, note (18)], that this time—amounting from 0·17 to 1·05 sec. in his first paper, and from 0·6 to 0·9 sec. in his last—will contribute only a very little to the age of the surface of the drops, new surface continually being formed during this time. This circumstance does

not, however, seem to me sufficiently to justify the neglecting of this, in this connection, very long time. I should rather be inclined to agree with the opinion set forth in his former paper, according to which the time for the formation of the drops is considered a measure for the age of the surface (*loc. cit.*, p. 233).

A comparison between the experiments of Prof. Lenard (*ibid.*, p. 236) and of Lord Rayleigh* on the surface-tension of a solution of soap seems also distinctly to show that the time of formation of the drops has a great influence on the condition of the surface. By the experiments of Lord Rayleigh with vibrating jets, the surface-tension of a solution of soap, 1/100 second after the formation of the surface, was thus found to be very near to that of pure water; while Prof. Lenard by experiments with vibrating drops (time of formation greater than $\frac{1}{4}$ sec.) finds the surface-tension of a soap solution of corresponding strength (1:1000) less than half that of water and rather near the stationary value of the surface-tension of a soap solution.

It appears, from the preceding, that the high values of the tension of a recently formed water-surface and the rapid decreasing of this value, which Prof. Lenard has found by his experiments, are not in agreement with the result of my previous experiments, because the tension of water-surfaces of lower age than those investigated by Prof. Lenard have been found much smaller and perfectly constant within the time interval (from 0·06 to 0·11 second after the formation of the surface) during which the method allowed the determination of the tension.

The cause of the great deviation between the results found by the method of drop-vibration and those found by the method of jet-vibration must, in my opinion, be sought in the circumstance that sufficient regard as to the influence of irregularities of mechanical character, arising from the disengagement of the drops, is scarcely taken by the drop method. The investigation of the influence of such irregularities seems also much more difficult by vibrating drops than by vibrating jets, the investigation by the latter being very much facilitated by the perfectly steady character of the phenomenon.

Concluding these remarks, I might call attention to the good agreement between the value of the tension of a water-surface 0·06 second old (73·23 dyne/cm. at 12° C.), found in my paper, and values of the tension of a water-surface found by statical methods† (Volkmann‡ 73·72 dyne/cm. at

* 'Roy. Soc. Proc.,' 1890, vol. 47, p. 281.

† As to the result found by other methods, I might refer to the discussion in my former paper (*loc. cit.*, pp. 314—317).

‡ 'Wied. Ann.,' 1896, vol. 56, p. 457.

12° C., Eötvös* 73.06). This agreement seems to show that the tension of a water-surface already only 0.06 second after the formation of the surface (and according to what is discussed in the present paper probably much earlier) has assumed the constant value which the tension, if contaminations are kept away, will retain during a very long time.

The Tidal Observations of the British Antarctic Expedition, 1907.

By SIR GEORGE DARWIN, K.C.B., F.R.S.

(Received September 27,—Read November 10, 1910.)

The present investigation was undertaken at the request of Sir Ernest Shackleton; the expense of the reduction was defrayed by him, and this paper is now communicated to the Royal Society by his permission. It will ultimately be republished as a contribution to the volume of the physical results of the expedition.

The first section, describing the method of observing, is by Mr. James Murray. The second section explains the reduction of the observations and gives a comparison between the new results and those obtained by the "Discovery" in 1902-3. The third section is devoted to the discussion of certain remarkable oscillations of mean sea-level and to speculations as to their cause and meaning.

I.—ON THE METHOD OF OBSERVING THE TIDES.

Early in June, 1908, preparations were begun for the erection of a tide-gauge, the most important feature of which was to be a recording apparatus made from a modified barograph. Owing to various delays and mishaps it was not before the middle of July that the gauge was completed in its final form, and the continuous record begun, which was carried on for more than three months, subject only to the loss of half an hour weekly, while the paper was being changed.

Dr. Mackay undertook the erection of the instrument, the apparatus was devised by the joint suggestions of Messrs. David, Mackay, Mawson, and Murray, while Mr. Day did the more delicate part of the work, namely, the alteration of the barograph.

* 'Math. es Természettud.,' 1885, vol. 3, p. 54 (Budapest).

The diagram (fig. 1) shows the chief parts of the apparatus and their relations to one another. The ice is shown in section, with the tripod and recording apparatus erected on it. A weight A, consisting of a box filled with stones, rests on the sea bottom. A piece of iron tubing B is let through the ice vertically and fastened. It is filled with paraffin oil, the object of which is to prevent the wire being frozen in, an idea used with success by the officers of the "Discovery." A wire C is taken from the weight on the sea bottom, passed through the oil-filled iron tube B, over the pulley D, and fixed to the end of the bamboo lever E, where it is kept

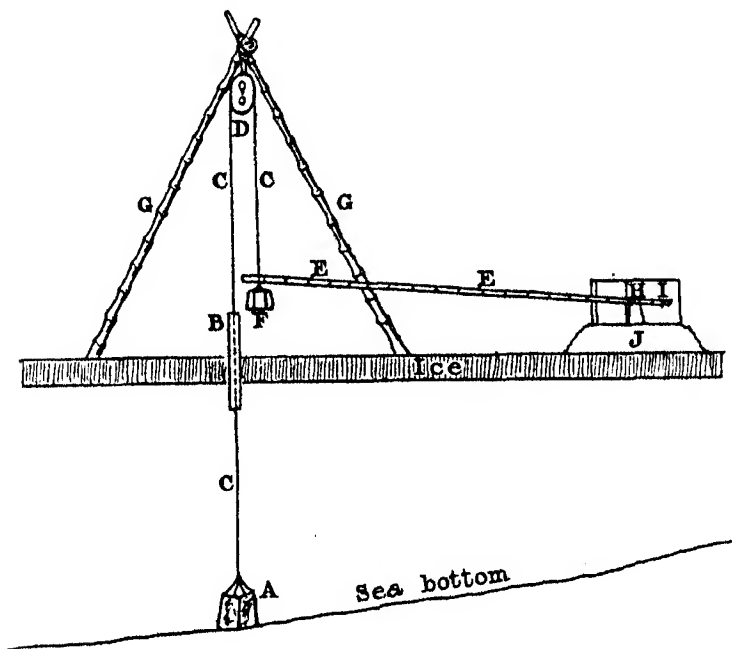


FIG. 1.

taut by the smaller weight F. The pulley D is suspended from a tripod of bamboo poles, of which two legs G are shown. The long lever E works on a spindle at H, and its short end I is connected by a cross-piece with the pen of the barograph. The details of this part are too small to be shown in this diagram, and will be illustrated in another figure. From this diagram there are omitted several parts, such as the guides which prevent the long lever from swinging during a blizzard, which are not essential to the understanding of the instrument. The barograph was of necessity covered by a box to keep out the snow. The lever entered through a slit in the end of the box, and an arrangement of canvas kept the snow out. The box containing

the barograph was raised on a little mound of snow J, in order to give the lever equal play above and below, or in other words, to allow of the mean sea-level being recorded about half-way up the drum. Of course the mean level had to be ascertained by a little observation.

The second diagram (fig. 2) is a plan on a larger scale of the recording part of the apparatus. The circle A is the drum of the barograph; B is the pen making the tracing on the drum; C is the axle on which the lever bearing the pen works. This lever is continued beyond the axle to a distance rather greater than that of the part bearing the pen. This end of the lever D is made much heavier than the other. The long bamboo lever E, of which only a small part is shown, is borne on an axle F, which is in line

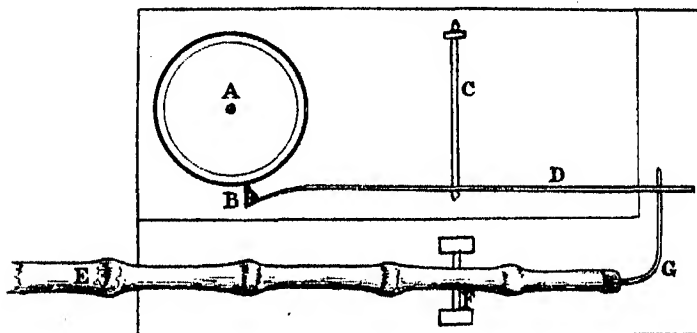


FIG. 2.

with the axle C in the barograph, though of course quite unconnected with it, being outside the glass box of the barograph. Attached to the end of the bamboo is a stout wire G, bent round so that it passes under the end D of the pen lever, which rests upon it by its own weight, and rises and falls with it, but, being quite free from it, is not affected by any vibration of the bamboo under the influence of the wind. The barograph pen has, of course, been uncoupled from the aneroid capsules, which are not indicated in the plan.

Dr. Mackay, with much assistance from Prof. David, had the tide-gauge set up, all but the recording part, by June 22. In order to utilise the facilities we now had for noting the changes of level, while waiting for the recording instrument to be finished, Dr. Mackay devised a very simple arrangement for ascertaining the amount of the tide. It was simply an inclined plane on which a paper marked with lines an inch apart was pinned. On this there slid a heavy block of wood which was attached to the end of the wire coming over the pulley. A lead pencil was inserted through a hole in the block of wood, which was kept in position by two guides.

This arrangement is shown in fig. 3, which is drawn in perspective. The pulley A is suspended from the tripod B, B, B. The wire C is attached to the wood block D, which slides on the inclined board E between the guides F, F. The pencil G is fixed so as to project a little below the block of wood; H is the line traced by the pencil.

This simple device was not intended to give anything but a straight line but it was hoped by frequent inspections to ascertain the turn of the tide,

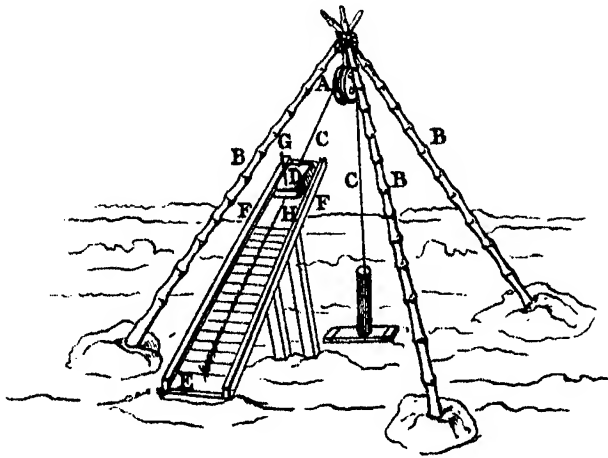


FIG. 3.

and Dr. Mackay kept vigil one night, and visited the gauge at intervals of about an hour.

Owing to a general slackness of the parts of the instrument the line traced was not a straight line, but a zigzag one, which proved of much greater interest. The pencil in descending did not follow the same course as it made going up, but swerved a little, and thus we got the first indications of what we believe to be seiches, at any rate of regular oscillations of much shorter intervals than those of the tides. The tracing obtained thus accidentally was too vague to enable us to count with certainty the number of periods per hour, but at any rate it demonstrated oscillations of a period of a few minutes and an amplitude of a few inches.

A number of records were taken in this rough manner till July 3, when the wire was found to be broken. A new situation was then selected for the tide-gauge, nearer the house, about 100 yards from shore, where the depth was 13 fathoms. The ice being now of considerable thickness, it was with no little labour that Dr. Mackay, with the help of Mr. Marston, got a new hole made to put the weight down.

By July 8 the apparatus was completed at the new place, this time with the recording attachment. A preliminary record was got from July 8 to 11, and the instrument was then stopped for readjustment. On July 14 it was finally started, and ran without mishap till nearly the end of October.

Prof. David usually changed the papers weekly. It was impossible to do this in the field, as it required bare hands. The barograph was therefore disconnected and carried to the house, where a new paper was put on and fresh ink put in the pen. The whole changing did not take more than half an hour.

The scale on which the curve was traced was about one-nineteenth of actuality—the long end of the lever being 11 feet and the short end 7 inches. The value of the factor of reduction of amplitude has therefore been taken to be $7/132$ or $1/18.857$.

One of the first records for a complete week was analysed. The curve appeared a simple one with one maximum daily, but a slight flattening of the minima indicated that other elements were present. The analysis showed that there was a smaller tide, having two maxima daily. The whole range of the tide at its highest was about 3 feet. The greatness of it surprised us, as the tide cracks usually showed a difference of level of not more than from 1 foot to $1\frac{1}{2}$ feet. This may have been because the free edge of the crack had not room to sink to the full extent of the tide, but came on bottom, and the ice then sagged away to the level part.

Towards the end of October the tripod was blown down during a blizzard, and the wire was snapped. The ice was by this time so thick that it was found impracticable to cut another hole to put a weight down, and so the observations were discontinued.

The curve traced on the drum gave very frequent indications of seiches in the form of festooning, but the scale was so small and the clock-motion so slow that these indications were blurred and useless for study. It was intended, and would have been easy, to substitute a clock of about 10 times the speed belonging to a Callendar recorder which we had with us, but it was late in the season before we could try it, and the breaking of the wire put a stop to the attempt.

II.—THE REDUCTION OF THE TIDAL OBSERVATIONS.

The motion of the ice carrying the tide-gauge relatively to the sea-bed was transmitted to the drum by means of a lever, as explained above. Accordingly, it is very nearly exactly the chord of the arc turned through by the lever which ought to have been measured. Yet it is the arc itself which is recorded on the curvilinear scale on the drum. The angle turned through

by the lever is, however, sufficiently small to permit us safely to neglect the correction in strictness required for the conversion of arcs to chords, and the arcs have been accepted as giving the changes of water level with sufficient accuracy.

The tidal record extended from July 14 to October 25, 1908, but the sheet which bore the record from October 12 to 18 is missing, and the record actually treated ends with October 11.

It was possible by means of a few interpolations to obtain an unbroken record from 0 h. astronomical time of July 14 to 23 h. of October 11. About an hour was generally lost once a week, while the paper was being changed, but it was always easy to complete the curve over this short interval by a pencil line, and this was regarded as equivalent to the actual curve.

On September 13 the pen failed to mark, but the curves on the 12th and 14th were unusually regular in character, so that a good interpolation for the 13th was easily obtained. The following is a list of the interpolated readings, and the hours are given inclusively in astronomical time:—

July 14, 0 h. to 3 h. (extrapolated); July 19, 19 h. to 23 h.; September 12, 17 h. to 23 h.; September 13, 0 h. to 23 h.; October 11, 22 h. and 23 h.

The errors of the clock do not seem to have been great enough to demand attention, and in fact, they are not always noted on the diagrams.

The clock was kept to apparent time, and was reset as the equation of time changed sensibly. But the scheme of reduction assumes that mean time has been used. This error may be taken into account with sufficient accuracy by certain changes in the true longitude of the place of observation, which was $166^{\circ} 12' \text{ E.}$

The observations were broken into three groups of a month each, for which the epochs were: (1) 0 h., July 14; (2) 0 h., August 13; (3) 0 h., September 12, 1908.

To allow for the equation of time the longitude for the first month was taken as 6 m. of time or $1^{\circ} 30'$ further east than in reality; in the second month the longitude was regarded as correct, and in the third it was shifted 10 m. or $2^{\circ} 30'$ to the west. The correction for the last month is less satisfactory than for the other two, because at that time of year the equation of time is changing rapidly, and differs considerably at the beginning and end of the month.

The unit adopted in tabulating the height was $1/10$ of an inch of the scale on the drum. Since 1 inch on the drum corresponds to 18.857 inches of water, the heights as derived from the harmonic analysis of the drum readings were converted to inches on multiplication by 1.8857.

For the tides M and O the observations were also treated as appertaining to a single period of three months, without regard to the equation of time; and a similar treatment was also extended to the tides S, K₂, K₁, and P₂ as will be explained more fully hereafter.

The reductions were made, under my supervision, by Mr. F. Finch with my apparatus,* and in the first instance the three months were discussed independently. The semidiurnal tides were derived from months of 30 days, and the diurnal tides from months of 27 days. In this treatment it is necessary to assume that the phase of the tide K₂ is the same as that of S₂, and that the amplitude of K₂ is 3/11ths of that of S₂. Similarly, we must assume identity of phases for K₁ and P, and that the amplitude of P is 1/3rd of that of K₁.

The following are the results:—

	1. July 14— Aug. 11.	2. Aug. 12— Sept. 11.	3. Sept. 12— Oct. 11.
M ₂	H = 2.55 in. $\kappa = 357^\circ$	2.64 in. 11°	2.11 in. 5°
S ₂	H = 1.08 in. $\kappa = 293^\circ$	1.21 in. 282°	1.20 in. 267°
K ₂	H = 0.29 in. $\kappa =$ Same	0.33 in. as for K ₂ .	0.33 in.
K ₁	H = 7.66 in. $\kappa = 6^\circ$	8.57 in. 9°	10.06 in. 10°
P	H = 2.56 in. $\kappa =$ Same	2.86 in. as for K ₁ .	3.35 in.
O	H = 6.95 in. $\kappa = 350^\circ$	7.94 in. 5°	8.68 in. 358°

In these results there appears to be some evidence of a progressive change as the season advances, such as was noted in the case of the observations made by the "Discovery" in 1902-3†, and I shall return later to this subject. But in the case of the tides S₂, K₂, K₁, P, this might easily arise from an erroneous assumption as to the heights and phases of K₂ and P relatively to those of S₂ and K₁ respectively. It is therefore advisable to discuss these tides without making the assumptions which are necessary when each month is treated quite independently of the others.

* 'Roy. Soc. Proc.,' 1892, vol. 52, p. 345, or 'Scientific Papers,' vol. 1, Paper 6.

† 'National Antarctic Expedition, 1901-4, Physical Observations' (1908), p. 6; or my 'Scientific Papers,' vol. 1 (1907), Paper 12.

In explaining my procedure, I adopt the notation of my paper "On an Apparatus for Facilitating the Reduction of Tidal Observations."*

The heights and phases of the tides S_2 , K_2 , K_1 , P are denoted respectively by H_s, κ_s ; H'', κ'' ; H', κ' ; H_p, κ_p .

The pair of harmonic constituents for diurnal tides, when 27 consecutive days are analysed, are denoted by $\mathfrak{A}_1, \mathfrak{B}_1$, and the theory shows that

$$\left. \begin{matrix} \mathfrak{A}_1 \\ \mathfrak{B}_1 \end{matrix} \right\} = \frac{f'H'}{\mathfrak{F}_1} \cos(\kappa' - V' - 13^\circ.29) - \frac{H_p}{\mathfrak{F}_1} \cos(\kappa' - V' - 13^\circ.29 + 2h_o - \nu' + 26^\circ.58 + \kappa_p - \kappa').$$

Similarly, when 30 consecutive days are analysed, and when P denotes the mean value for the month of the ratio of the cube of the sun's parallax to his mean parallax, the pair of semi-diurnal constituents are given by

$$\left. \begin{matrix} \mathfrak{A}_2 \\ \mathfrak{B}_2 \end{matrix} \right\} = PH_s \cos \kappa_s + \frac{f'H''}{\mathfrak{F}_2} \cos(\kappa_s - 2h_o + 2\nu'' - 29^\circ.53 + \kappa'' - \kappa_s).$$

In treating each single month independently, we assumed $\kappa_p = \kappa'$, $\kappa_s = \kappa''$, $\frac{H_p}{H'} = \frac{1}{3}$, $\frac{H''}{H_s} = \frac{3}{11}$, but we now no longer make that supposition.

If we put

$$\left. \begin{matrix} a' \\ b' \end{matrix} \right\} = \frac{f'}{\mathfrak{F}_1} \cos(V' + 13^\circ.29); \quad \left. \begin{matrix} a_p \\ b_p \end{matrix} \right\} = \frac{1}{\mathfrak{F}_1} \cos(V_p - 13^\circ.29);$$

$$\left. \begin{matrix} A' \\ B' \end{matrix} \right\} = H' \cos \kappa'; \quad \left. \begin{matrix} A_p \\ B_p \end{matrix} \right\} = H_p \cos \kappa_p;$$

a' , b' , a_p , b_p , are known functions, and each month gives the pair of equations—

$$\begin{aligned} \mathfrak{A}_1 &= a'A' + b'B' + a_pA_p + b_pB_p, \\ \mathfrak{B}_1 &= -b'A' + a'B' - b_pA_p + a_pB_p. \end{aligned}$$

Thus the three months afford six equations for the determination of A' , B' , A_p , B_p , from which the heights and phases of K_1 and P are easily found.

Again, if we put

$$\begin{aligned} a_s &= P; & \left. \begin{matrix} a'' \\ b'' \end{matrix} \right\} &= \frac{f''}{\mathfrak{F}_2} \cos(V'' + 29^\circ.53); \\ b_s &= 0; \\ \left. \begin{matrix} A_s \\ B_s \end{matrix} \right\} &= H_s \cos \kappa_s; & \left. \begin{matrix} A'' \\ B'' \end{matrix} \right\} &= H'' \cos \kappa''; \end{aligned}$$

each month gives for the semi-diurnal tides the pair of equations—

$$\begin{aligned} \mathfrak{A}_2 &= a_sA_s + b_sB_s + a''A'' + b''B'', \\ \mathfrak{B}_2 &= -b_sA_s + a_sB_s - b''A'' + a''B''. \end{aligned}$$

* 'Roy. Soc. Proc.' 1892, vol. 52, pp. 345–380; or 'Scientific Papers,' vol. 1 (1907), Paper 6.

and the three months give six equations for determining A_s , B_s , A'' , B'' , from which the heights and phases of S_2 and K_2 are easily found.

On solving the diurnal group of equations by least squares, I find $H' = 8.311$ inches, $\kappa' = 11^\circ 50'$, $H_p = 1.795$ inch, $\kappa_p = 12^\circ 11'$. The ratio of H' to H_p is 4.63, instead of the 3 assumed from theoretical considerations in the separate treatment of the months, but the phases are virtually identical. The similar treatment of the semi-diurnal group gives

$$H_s = 0.938 \text{ inch, } \kappa_s = 273^\circ 25'; H'' = 0.584 \text{ inch, } \kappa'' = 257^\circ 35'.$$

The ratio of H_s to H'' is 1.605, instead of $3\frac{1}{2}$, as assumed from theory.

It thus appears that the theoretical hypotheses were considerably in error, and results probably more in accordance with the truth will be obtained from the several months if we assume

$$H' = 4.63 H_p, \kappa_p - \kappa' = 0^\circ 22'; H_s = 1.605 H'', \kappa_s - \kappa'' = 15^\circ 50'.$$

With these assumptions the three months now give—

	1.	2.	3.
K_1	$H = 8.20 \text{ in.}$ $\kappa = 10^\circ$	8.31 in. 16°	8.58 in. 10°
P	$H = 1.77 \text{ in.}$ $\kappa = 11^\circ$	1.79 in. 17°	1.85 in. 11°
S_2	$H = 0.96 \text{ in.}$ $\kappa = 272^\circ$	0.93 in. 276°	0.94 in. 272°
K_2	$H = 0.60 \text{ in.}$ $\kappa = 256^\circ$	0.58 in. 260°	0.59 in. 256°

The appearance of progressive seasonal change in this group of tides has now almost disappeared, although the middle month is slightly discordant from the other two.

It is interesting to note that, in the result of the treatment by least squares, κ' (for K_1) is practically identical with κ_p (for P), but that there is a considerable divergence between κ_s (for S_2) and κ'' (for K_2).

The difference between the phase of M_2 (which we may take as given by $\kappa_m = 5^\circ$) and that of S_2 given by $\kappa_s = 273^\circ$ is very large, although their difference of speeds is not great. Hence we should expect that a small difference of speed in a semi-diurnal tide would make a sensible difference in phase.

If phase varies simply as difference of speed, we shall have the following results:—

Speed of S_2 —speed of $M_2 = 1^\circ.016$ per hour; $\kappa_s - \kappa_m = 273^\circ - 365^\circ = -92^\circ$.

Speed of K_2 —speed of $S_2 = 0^\circ.082$ per hour.

Hence we ought to find

$$\frac{\kappa'' - \kappa_s}{\kappa_s - \kappa_m} = \frac{0.082}{1.016}, \quad \text{or} \quad \kappa'' = \kappa_s - \frac{82}{1016} \times 92^\circ = \kappa_s - 7^\circ.$$

As a fact, we find $\kappa'' = \kappa_s - 16^\circ$, and thus the direction of the difference of phases is such as was to be expected, although the amount is not quite satisfactory. With tides of such small amplitude, however, and with only three months on which to rely, the amount of agreement is all that is to be expected.

The results of the analysis for the tides M_2 and O , when the months are taken independently, are given above. If, however, we neglect the equation of time, the whole period of three months may be treated as a single group of observations. In this way I obtain for M_2

$$\begin{aligned} H_m &= 2.4233 \text{ inches,} \\ \kappa_m &= 5^\circ 33'. \end{aligned}$$

If we take the three values of each of the quantities $H_m \cos \kappa_m$, $H_m \sin \kappa_m$, from our previous results, and form means of these functions, we obtain

$$\begin{aligned} H_m &= 2.4183 \text{ inches,} \\ \kappa_m &= 4^\circ 20'. \end{aligned}$$

The latter method has the advantage that it takes the equation of time into account; the former is somewhat more likely to eliminate casual inequalities. We may safely take $H_m = 2.42$ inches, $\kappa_m = 5^\circ$, as being very near the truth.

Similarly the whole series when treated for the O tide gives

$$\begin{aligned} H_o &= 8.1645 \text{ inches,} \\ \kappa_o &= 1^\circ 0'. \end{aligned}$$

But the means of the three values of $H_o \cos \kappa_o$, $H_o \sin \kappa_o$, give the somewhat discordant result

$$\begin{aligned} H_o &= 7.8407 \text{ inches,} \\ \kappa_o &= 359^\circ 45'. \end{aligned}$$

I should have expected the two evaluations to be closer together, as was the case with M_2 , and I think we must accept

$$\begin{aligned} H_o &= 8.0 \text{ inches,} \\ \kappa_o &= 0^\circ. \end{aligned}$$

as being as nearly accurate as is possible from our data.

In the reduction of the "Discovery" observations it was known that there had frequently been a small change of the zero point in consequence of the shift in the ship, and I did not think it was worth while to attempt

to combine the several months by least squares so as to separate the tides S_2 from K_2 , and K_1 from P . I now think that it was a pity that the attempt was not made to separate them, and therefore I have gone back to the old work and discussed the numbers by least squares with the results given below. In the course of this revision it appeared that there had been a small mistake in the value assigned to P for each month, which, however, made little change in the values assigned to the tide S_2 , and did nothing to remove the considerable discrepancies between the results from each of the 12 months.

FINAL TABLE OF RESULTS FOR "NIMROD," TOGETHER WITH COMPARISON WITH "DISCOVERY."

"Nimrod," 1908.		"Discovery," 1902—3.	"Discovery," new reduction.
M_2	$H = 2.42$ in. = 0.202 ft. $\kappa = 5^\circ$	1.966 in. = 0.164 ft. 10°	
S_2	$H = 0.94$ in. = 0.078 ft. $\kappa = 273^\circ$	1.142 in. = 0.095 ft. 272°	1.129 in. = 0.094 ft. 272°
K_2	$H = 0.584$ in. = 0.049 ft. $\kappa = 255^\circ$	0.311 in. = 0.024 ft. 272°	0.396 in. = 0.033 ft. 294°
K_1	$H = 8.31$ in. = 0.693 ft. $\kappa = 12^\circ$	9.245 in. = 0.770 ft. 14°	10.177 in. = 0.848 ft. 14°
P	$H = 1.795$ in. = 0.150 ft. $\kappa = 12^\circ$	3.082 in. = 0.257 ft. 14°	3.228 in. = 0.269 ft. 3°
O	$H = 8.0$ in. = 0.67 ft. $\kappa = 0^\circ$	9.264 in. = 0.772 ft. 0°	

The agreement between these two sets of constants, deduced from observations taken at places some 25 miles apart, seems to be very good. The later observations were taken further north than the earlier ones, and the greater value of M_2 in the more northerly series is probably a reality. The two days of observation made by Dr. Wilson in 1904 close to the "Nimrod" station agree with our present results in indicating a slightly increased value of the semi-diurnal tide.

In discussing the "Discovery" tides, I was led to suspect that there were semi-diurnal nodal lines to the northward, but that the node for S_2 was nearer than that for M_2 . The fall in the amplitude of S_2 agrees with this, and possibly the amplitude of M_2 has begun to increase as we go northward previously to its subsequent decrease to the zero value at the node.

The ratio of M_2 to S_2 for "Nimrod" is 2.57, and for "Discovery" 1.74; the former value is more nearly normal than the latter.

The sums of the heights of M_2 , S_2 , K_2 , are respectively 3.94 inches for "Nimrod" and 3.49 for "Discovery."

The sums for K_1 , P , O are 18.1 inches for "Nimrod" and 22.7 inches for "Discovery." Thus for "Nimrod" the greatest diurnal tides are 4.6 times as great as the greatest semi-diurnal tides, while for "Discovery" the greatest diurnal tides are 6.5 times as great as the greatest semi-diurnal tides. This again emphasises the diminishing importance of the semi-diurnal tides as we penetrate to the south.

It should be remarked that the difference of phase of K_2 from that of S_2 in the new reduction for "Discovery" is not in accordance with the theoretical considerations adduced in support of the corresponding difference for "Nimrod." However, too much stress should not be placed on results derived from these very small tidal oscillations.

On the whole, I conclude that we now know the tidal constants at this part of the Antarctic Ocean with as much accuracy as is desirable, and I refer the reader to the discussion of the "Discovery" observations for the conclusions which may be drawn from the values found.

In discussing the "Discovery" observations, I saw reason to suspect a remarkable seasonal change in the amplitude and phase of the tide M_2 ; it is therefore interesting to see whether these new observations tend to confirm that conclusion. The results in my previous paper were discussed by means of curves, but I will now merely examine the matter numerically.

The results for each month which has been reduced, viz., 12 for "Discovery" and 3 for "Nimrod," may be held to appertain to the middle of the month under consideration, that is to say 15 days after the corresponding epoch.

The following table exhibits the values of H_m and κ_m for each of the

Date.	H_m .	κ_m .
	inches.	°
Apr. 21, 1903.....	1.91	-12
May 24, 1903.....	2.20	-5
" 27, 1902.....	2.27	1
June 20, 1902.....	2.29	2
" 30, 1903.....	2.33	4
July 29, 1903.....	2.41	9
* " 29, 1908.....	2.55 (2.08)	-5
Aug. 8, 1902.....	2.18	14
* " 28, 1908.....	2.64 (2.15)	11
" 29, 1903.....	2.18	15
Sept. 7, 1902.....	1.93	22
* " 27, 1908.....	2.11 (1.72)	5
Oct. 8, 1902.....	1.74	26
" 28, 1902.....	1.56	32
Nov. 28, 1902.....	1.21	31

15 months, together with the dates to which they may be held to apply. The new results are marked with an asterisk.

In order to judge of the progression in the heights, we should note that the mean H_m for the northern place is 2.42, and for the southern is 1.97. Hence we ought, perhaps, to reduce the three heights for "Nimrod," viz., 2.55, 2.64, 2.11, in the proportion of 197 to 242. The corresponding numbers, as so reduced are written in parentheses after the actual numbers. The progression in the heights appears to be fairly consistent, but that of the phases is not nearly so clear. The phase of the first of the "Nimrod" months is some 15° away from what we should expect if the progressive change is an actuality. If we convert this into time, it means that the high water should be changed by about half an hour to fit into the supposed progression. The middle month fits into its place fairly well, but the high water for the third month should be shifted some 40 minutes. Such changes are not, however, large, when we consider that the range from high to low water is only about 5 inches. On the whole, I should say that the new results do not tend to confirm the truth of the progressive change in any marked degree, but they can hardly be held to invalidate it.

If we examine the results of the three months for the O tides, we find some traces of a seasonal progression, for the heights are 6.95, 7.94, 8.64; but the progression of phases is again not clearly marked, for they are -5° , $+5^\circ$, -2° . I was not able to detect any evidence of progression in the case of the O tide as observed by the "Discovery."

III.—ON SEA-SEICHES IN THE ANTARCTIC OCEAN.

In the course of the reduction of the tidal observations the mean daily heights of the water were computed, so as to furnish a cross verification of the summations necessary in the harmonic analysis. In view of the arduous conditions under which the observations were made it also seemed well to test the series of means, so as to detect any accidental shift in the zero of the gauge which might have occurred. Unfortunately, no such systematic examination of the "Discovery" observations had been carried out, because it was well known that there had been frequent small changes of zero due to the shift of the ship. It did not occur to me that a graphical illustration of mean sea-levels, known to be subject to somewhat frequent changes of zero, might give indications of anything worthy of notice.

A cursory examination of a table of the daily mean sea-levels of the present series at once revealed considerable inequalities. The paper on the drum was changed once a week, yet there was no sign of any weekly discontinuity, and the observers did not think there was any reason to suspect a change between

each paper and the next. A zigzag of daily mean sea-levels was accordingly plotted, as shown on a reduced scale in the firm line of fig. 4. I was surprised to see a somewhat regular rise and fall of the water with a period of about three days, for nearly five weeks on end. Although the rise and fall was then interrupted, this seemed to be a fact worth looking into.

A line drawn so as to bisect the zigzags clearly undergoes changes of considerable amount, for which it is only possible to guess the causes. Distant barometric changes and distant gales may be responsible for most of the effect. There are also probably annual and semi-annual meteorological tides, fortnightly and monthly astronomical tides, and some small apparent inequality with a period of a fortnight due to the residual effects of the tides of short period. But these causes obviously could not produce the shorter zigzags, so that we may consider these as being embroidered, to use M. Forel's phrase, on a slowly variable curve.

Local barometric changes must affect the mean sea-level, and pressure above the mean will correspond with depressed sea-level, at the rate of about $13\frac{1}{2}$ inches of water to one of mercury, and *vice versa*. Mr. James Murray has given me the mean barometric heights both in a tabular and in a graphical form. The means of pressure are given in civil time, while those of sea-level were computed according to astronomical time. I therefore made a rough estimate from the curve of the mean pressure according to the latter time. The mean pressure for the 90 days of observation was then found, and a correction was applied to the sea-levels at the rate of 14 inches of water to one of mercury above or below the estimated mean. A rather high value for the correction is taken, because it seemed desirable to give the barometric changes every possible chance of annulling the sea changes; and further, because, by the use of the factor 19 (instead of 18.857), the zigzags had been very slightly exaggerated. In any case, the correction is quite exact enough for such a rough allowance for barometric pressure as is possible.

The corrected mean sea-levels are shown in the dotted curve of fig. 4. It will be seen that the zigzags are sensibly diminished, but not annulled, and that in one or two places a new maximum or minimum has been introduced. We may conjecture that distant barometric changes and distant gales may have annulled some maxima and minima which would otherwise have been visible.

For observations of this uncertain kind mathematical treatment for the detection of partially veiled periodicity seems inappropriate. I have therefore only examined the zigzag for maxima and minima and have noted these incidences in the following table. In five cases a mark of *quære* is

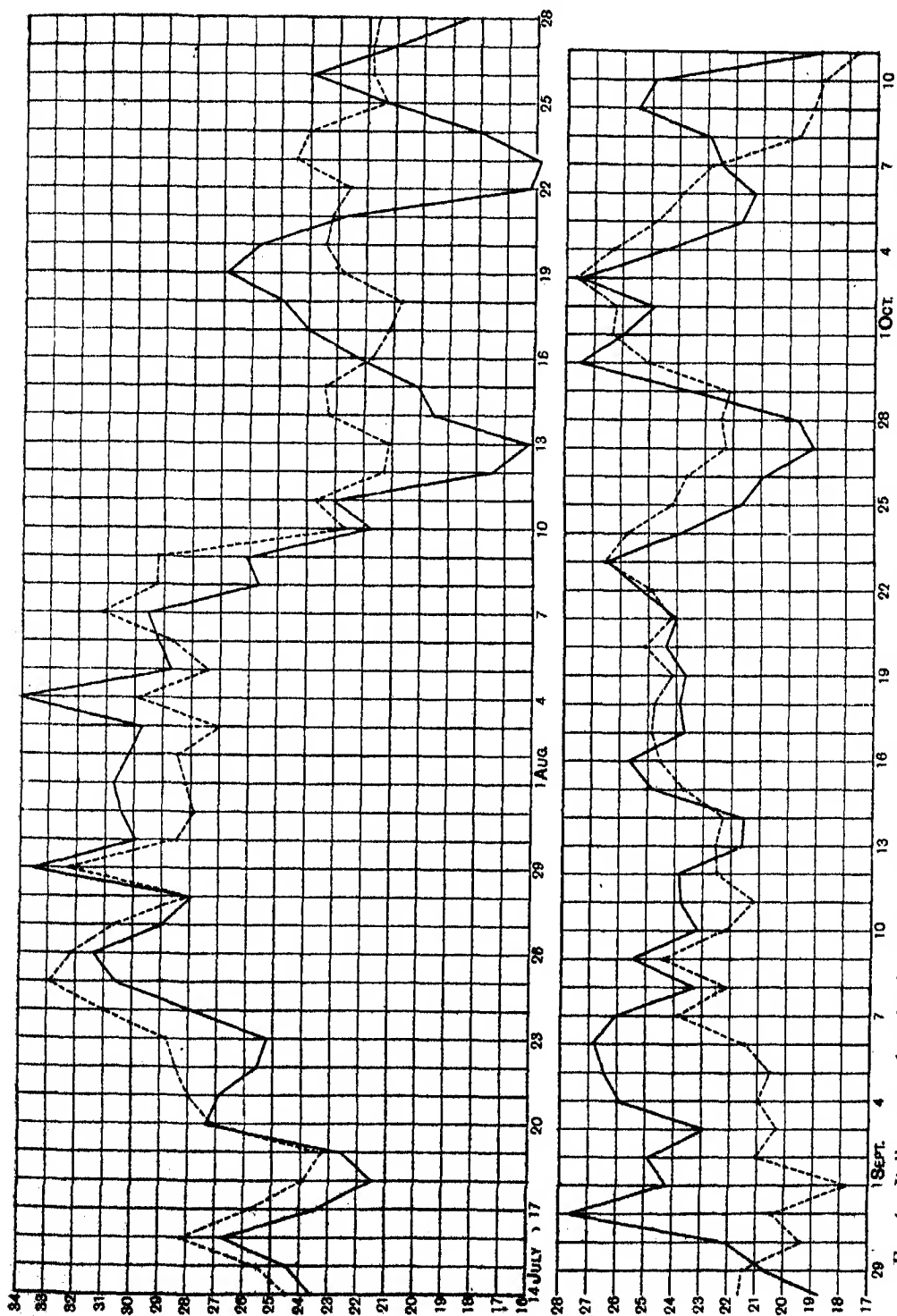


FIG. 4.—Daily means of sea-level, and the same corrected for barometric pressure, referred to an arbitrary zero and expressed in inches.

added because another observer might deny the existence of a maximum or minimum which I conceived to be there, but partially masked by the general rise or fall of an ideal line bisecting the zigzags of the dotted line. In the second column of each half of the table I give the differences between the dates in days, and these numbers will give the period of the suspected inequality.

TABLE OF MAXIMA AND MINIMA OF MEAN SEA-LEVEL CORRECTED FOR
BAROMETRIC PRESSURE, 1908.

Maxima.	Periods in days.	Minima.	Periods in days.
July 16	5	July 14	5
21	4	19	4
25	4	23	5
29	4	28	3
Aug. 2	2	31	3
4	3	Aug. 3	2
7	2	5	2
9	2	7	3
11	3½	10	3
14½	5½	13	5
20	3½	18	4
23½	3½	22	3
27	4	25	3
31	2	28 ?	2
Sept. 2	2	30	2
4	3	Sept. 1	2
7	2	3	2
9	3½	5	3
12½	4½	8	3
17	3	11	3
20	3	14	5
23	3	19	2
26 ?	2	21	3½
28	3	24½ ?	2½
Oct. 1	2	27	2
3	4	29	3
7 ?	3	Oct. 2	3
10		5 ?	3
		8	3
		11	3

The intervals between successive maxima are as follows:—

$$1 \text{ of } 5\frac{1}{2} = 5\frac{1}{2}$$

$$1 \text{ of } 5 = 5$$

$$1 \text{ of } 4\frac{1}{2} = 4\frac{1}{2}$$

$$5 \text{ of } 4 = 20$$

$$4 \text{ of } 3\frac{1}{2} = 14$$

$$7 \text{ of } 3 = 21$$

$$8 \text{ of } 2 = 16$$

$$\text{Total of 27 periods} = 86 \text{ days.}$$

$$\text{Mean period} = 3.185 \text{ days.}$$

If we suppose the intervals of $5\frac{1}{2}$, 5, and $4\frac{1}{2}$ were really double periods, with masked maxima intervening, there were 30 periods, and the mean becomes 2.867 days.

The intervals between the successive minima are as follows:—

4 of 5 = 20	
2 of 4 = 8	
1 of $3\frac{1}{2}$ = $3\frac{1}{2}$	Total of 29 periods = 89 days.
13 of 3 = 39	Mean period = 3.069 days.
1 of $2\frac{1}{2}$ = $2\frac{1}{2}$	
8 of 2 = 16	

If the intervals of five days were really double periods with masked minima intervening, there were 33 periods and the mean period becomes 2.697 days.

Taking both estimates as of equal weight we get a mean interval of 3.127 days, or allowing for possible masked maxima or minima, as explained above, of 2.782 days. I think then that there is some evidence of the existence of an oscillation with a period of about three days.

In a paper in the 'Philosophical Magazine' (January, 1908, p. 88), Messrs. Honda, Terada, and Isitani discuss "Secondary Undulations of Oceanic Tides" or sea-seiches. These seiches occur in bays, and they find that the period depends on the size and depth of the bay. In some bays the period is fairly constant, but in others it changes "continuously and through certain ranges." They show that for a bay of length l and depth h the main period T is given by the formula $4l \div \sqrt{gh}$, where g is gravity. The period as so computed is subject to a correction due to the opening into the sea, but as we only now want a very rough estimate of the period, the correction may be neglected. The formula is the same as that for the period of the uninodal seiche in a lake of length $2l$. The authors in fact regard the end of the bay as resembling the end of a lake, while the seaward opening is equivalent to the middle of the lake. Accordingly the second half of the lake, which would stretch out into the sea, is suppressed. The formula gives results in accordance with the seiches observed in many Japanese bays, and they remark that bays are also sometimes disturbed by seiches of shorter period, which they regard as transverse seiches from side to side of the bay, just as if it were an enclosed basin.

In none of the examples given by these authors has the seiche a period at all comparable with that of which we have reason to suspect the existence in the Antarctic Sea, but that affords no reason for refraining to apply the theory to such prolonged oscillations. In most inland lakes the seiches have periods of 10 minutes to one or two hours, yet in Lake Erie the seiche is found to have a period of 13 hours, while in the Lakes of

Michigan and Huron conjointly a seiche of 45 hours is suspected.* Thus we have justification for the application of the theory to oscillations of very long period.

In the case of the Antarctic Sea, if there is a great bay running far back into the Antarctic continent behind the ice barrier, its length and depth are quite unknown. Hence there are elements of great uncertainty in the application of the theory.

It seems likely, at any rate, that the bay extends for a considerable distance, and speculations have even been made as to whether there may not be an arm of the sea stretching through to the Weddell Sea almost diametrically across what was supposed to be a continent.

It might, perhaps, be thought that the thick ice of the barrier would serve to damp out oscillations of sea-level; but, unless, indeed, the sea is solid to the bottom, I conceive that the ice would behave like an elastic skin, and would hardly exercise any damping effect on oscillations with a period of more than an hour or two.

It seems almost impossible that the remarkable changes of sea-level which are observed should arise from errors of observation, and if they exist at Backdoor Bay, the neighbouring sea along the barrier must necessarily also partake of the motion. If the sea rises and falls, the barrier itself must move with it; and it may be suspected that it is subject to a true tidal rise and fall.

If we accept the existence of a sea-seiche with a period of three days, the formula gives some indication as to the length and depth of the bay behind the barrier. We cannot assume the sea to be very shallow, because if it were so it would inevitably be frozen solid to the bottom. Moreover, a shallow sea would certainly be broken up by shoals, so that it could not oscillate as a single system. A little consideration shows that to produce a seiche of three days the bay must be of enormous length, and for the reasons assigned it would be useless to assume it to be very shallow. The few soundings near the barrier give depths of between 200 and 300 fathoms, and perhaps a somewhat smaller depth might suffice to allow of the required seiche. I propose to guess the length of the bay and to find what depth of sea is required to produce a seiche of three-day period.

I guess then that the bay behind the barrier stretches past the South Pole and a little to the east of it as far as latitude 80° . Such an inlet would have a length of 25° to 30° of latitude. It seems likely that if it is really an arm of the sea through to Weddell's Sea, with a constriction about the place where we place the end of the bay, the seiche would be much the same.

* Dr. Anton Endrös, 'Petermann's Geograph. Mittheilungen,' Heft II, 1908.

The length of our supposed bay in centimetres will be 25 or 30 times $60 \times 1.852 \times 10^5$ cm., and these I take as two assumed values of l . On completing the multiplications I find that $4l$ will be $1\frac{1}{2} \times 10^9$ cm. or $1\frac{1}{2} \times 10^9$ cm.

The period of oscillation is three days, or 2.592×10^5 sec.; also g is 981. Thus, numbering our two alternatives as (1) and (2), we get:—

$$(1) \ 2.592 \times 10^5 = \frac{1\frac{1}{2} \times 10^9}{\sqrt{981h}}; \quad (2) \ 2.592 \times 10^5 = \frac{1\frac{1}{2} \times 10^9}{\sqrt{981h}}.$$

Whence

$$\begin{aligned} (1) \ h &= \frac{1}{981} \left(\frac{1\frac{1}{2} \times 10^9}{2.592} \right)^2 & (2) \ h &= \frac{1}{981} \left(\frac{1\frac{1}{2} \times 10^9}{2.592} \right)^2 \\ &= 18,732 \text{ cm.} & &= 26,975 \text{ cm.} \\ &= 102.4 \text{ fathoms.} & &= 147.5 \text{ fathoms.} \end{aligned}$$

Thus a sea of from 100 to 150 fathoms in such an immense bay as has been conjectured would oscillate with a period of three days, and the observed results are seen to be consistent with the existence of a deep inlet, almost or quite cutting the Antarctic continent in two.

Such a conclusion is interesting, but it would not be right to attribute to it a high degree of probability, because there are elements of uncertainty on every side.

In view of the interest of our result it has seemed well to revert to the observations made by Captain Scott's expedition, notwithstanding the known uncertainty in the zero of the gauge. I have therefore examined 175 days of the "Discovery's" record, viz., 113 days of 1902 and 62 days of 1903. No correction has been applied for barometric pressure, and thus periodic inequalities have doubtless sometimes been masked by contemporaneous changes of pressure, and perhaps by the shift of zero. Thus I should expect to find rather a larger proportion of long intervals between consecutive maxima and minima than in the "Nimrod" results as reduced for pressure. I found, in fact, on analysing the zigzag in the way already explained that, amongst the periods as deduced from maxima, there were:—

2 of 7 d., 1 of $6\frac{1}{2}$ d., 10 of 5 d., 1 of $4\frac{1}{2}$ d.,

and amongst the periods, as deduced from minima, there were—

1 of 9 d., 1 of $6\frac{1}{2}$ d., 4 of 6 d., 3 of 5 d., 1 of $4\frac{1}{2}$ d.

Taking maxima and minima together there were 83 periods amounting to 323 days, thus giving a mean period of 3.9 days.

But if we postulate that periods from 7 days to $4\frac{1}{2}$ days were really double periods with masked maxima or minima intervening, and that the

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9-day period is really triple, we get 105 periods for 323 days, with a mean of 3.1 days.

These results are generally confirmatory of the preceding ones, but seem to indicate a slightly longer period.

In this rough examination there is undoubtedly a danger of finding a false periodicity under the influence of unconscious bias. I thought it advisable therefore to examine other tidal records, for it might be possible to perceive periodicity even in cases where there was but small likelihood of its real existence. Colonel Burrard then kindly sent me tables of daily mean sea-levels for the year 1880 from May 1 to June 30 and from October 1 to November 30 for Aden, Karachi, Madras and Port Blair, Andaman Islands. These old observations were chosen because it had been usual at that time to have each daily mean "cleared" of the residual effects of the tides of short period, and thus one slight source of error was obviated. I also proceeded in the case of Aden to deduct the tides of long period, but as this correction clearly made no difference in the kind of inequality I was looking for, I did not carry out that laborious task in the other cases.

The tabulated numbers were then plotted out in a number of curves.

An imaginative investigator might possibly fancy he could detect signs of periodicity with a period of two or three days at Aden and at Port Blair, but as the range from crest to hollow was not more than $\frac{1}{2}$ inch, it seems safer to say that no periodicity could be traced.

In the curve for Madras there are considerable irregularities, but it seemed impossible even to imagine any periodicity. At Karachi there does seem to be an inequality with a period of two to three days and a range of two or three inches. A succession of waves with three to five crests one after the other is observable at several parts of the curve. It seems quite likely that sea-seiches may exist in the Indian Ocean, and Karachi would be well placed for observing them.

These Indian results were not corrected for barometric pressure, and it may be worth while hereafter to submit them to a more systematic examination. For the present, however, I am satisfied with the conclusion that periodicity is not to be seen in all cases, and that the oscillations of mean sea-level in the Antarctic Sea are many times as great as those in the Indian Ocean and Bay of Bengal. Thus it seems unlikely that imagination is responsible for the existence of the Antarctic sea-seiches, and we may hope that the investigations of Captain Scott's second expedition will throw some further light on the subject, and possibly also on the existence of a deep bay behind the barrier.

On a Mistake in the Instructions for the Use of a Certain Apparatus in Tidal Reductions.

By Sir G. H. DARWIN, K.C.B., F.R.S.

(Received November 4,—Read November 10, 1910.)

The apparatus is described in the 'Proceedings' of the Royal Society, 1892, vol. 52, p. 345 (or my "Collected Scientific Papers," vol. i, p. 216). I first correct an obvious misprint in fig. 3, where 24β is inserted in place of 24ϵ .

In § 6 the incidence is determined of the exact mean solar hours of a given day amongst the hours of a special time scale, when the 12 h. of solar time is assumed to fall within half a special hour of an exact hour of special time. Starting from this 12 h. of solar time we proceed upwards by subtracting 1, 2...12 hours of solar time, but expressed in special time, adding 24 h. to the integral special hours when necessary so as to make that integral number lie between 0 and 23 inclusive. Similarly we proceed downwards by adding 1, 2...11 hours of solar time expressed in special time, and similarly reduce the integral number of special hours so that it shall lie between 0 and 23. There are thus 24 lines in the schedule, 12 lying above the middle and 11 below.

If t denotes an exact solar hour, τ an exact special hour, and δ an error expressed in special time, each line of the schedule is of the form

$$t = \tau + \delta,$$

where both t and τ are whole numbers lying between 0 and 23 inclusive.

The frequency of the error δ is investigated, and is shown to conform to a certain law which is identically the same for each special hour from 0 to 23 inclusive.

Each harmonic tide goes through its period n times (with n equal to 1, 2, 3, 4, or 6) in its appropriate special day. The height of the water is supposed to be observed at the exact solar hours, and the problem is to determine the error in the result when the observations are deemed to appertain to the corresponding exact hours of special time.

M. M. H. van Beresteyn wrote to me from the Hague expressing his opinion that my procedure was erroneous, and I regret to find that his suspicion is well founded. Fortunately the error thus introduced is insignificant as regards practical tidal work.

I will not explain how I came to go wrong, but will consider the correct procedure and show how the rules of computation must be amended.

Let ω denote the speed of any one of the harmonic tides expressed in degrees per mean solar hour. Then since we may without loss of generality take the amplitude of the tide as unity and the phase as zero, the 24 observations at the mean solar hours will be 24 values of $\cos n\omega t$ corresponding to t equal to 0, 1, 2 . . . 23, and as before n is one of the numbers 1, 2, 3, 4 or 6. We might equally well have proceeded from $\sin n\omega t$ and it is on this account that the phase is immaterial for our discussion.

We have to translate $\cos n\omega t$ into special time. By the definition of a special day, ω when translated becomes 15° per special hour, and by the schedule of incidence t becomes $\tau + \delta$, thus we have

$$\cos n\omega t = \cos 15^\circ n(\tau + \delta).$$

In my paper I virtually wrote $15^\circ \tau$ as θ , and $15^\circ \delta$ as x , so that x was error reduced to angular measure at the rate of 15° per special hour.

Hence the function to be considered is $\cos n(\theta + x)$, where x is subject to a certain known law of frequency, say $f(x)$.

It was at this point that I made the mistake, for I erroneously considered the function $\cos n(\theta - x)$.

The required mean value of $\cos n(\theta + x)$ is clearly to be determined from the fraction

$$\frac{\int_{-\infty}^{+\infty} f(x) \cos n(\theta + x) dx}{\int_{-\infty}^{+\infty} f(x) dx}.$$

The integral in the denominator was found correctly, but that in the numerator was wrong because of the wrong sign of x under the cosine.

The factor in the result which was given as $\cos n[\theta - \frac{1}{2}(a-b)]$ must be corrected so as to stand as $\cos n[\theta + \frac{1}{2}(a-b)]$.

It is proved that $a-b$ is equal to ϵ , where

$$\epsilon = 15^\circ \left[1 - \frac{\text{m. s. day}}{\text{special day}} \right].$$

The correct final result is

$$\frac{1}{\mathfrak{F}_n} \cos n(\theta + \frac{1}{2}\epsilon).$$

The \mathfrak{F}_n was correct, but the term in ϵ was given in the paper with the wrong sign.

Accordingly the paper may be corrected by changing the sign of every term involving ϵ and in the computation forms the corrections in ϵ have been applied with the wrong sign although the numerical values remain correct.

Copies of the computation forms have been sold by the Cambridge Scientific Instrument Company for use with the apparatus, and I shall try to

reach the purchasers by circular pointing out that all the corrections on p. 12 of the forms which involve ϵ have been systematically applied with the wrong signs. I notice on p. 12 under the heading M_3 a misprint of $\frac{1}{2}\epsilon$ instead of 3ϵ , but the number attached, viz., $1^{\circ}57$ is correct, except of course as to its sign.

The correction of the phases κ derived from the erroneous instructions may be at once effected without recurring to the original computations by adding to each κ twice the value tabulated in the paper for the corresponding $\frac{1}{2}\eta\epsilon$.*

If this note should be seen by anyone concerned who may not receive a circular I beg him to notice the correction.

It has already been remarked that the error is practically insignificant. The only tide in which it could possibly be appreciable is M_2 , and since in this case the correction ϵ is equivalent to one minute of time in high water, the mistake caused by the erroneous instructions has been two minutes of time or 1° in κ . Even for M_2 the discrepancies in κ from year to year are often as great or greater than 1° , and in the smaller tides they are frequently far greater; moreover the solar group of tides has been unaffected by the mistake.

Although practically the error is of little importance, it is clear that it ought to be corrected.

* See 'Roy. Soc. Proc.,' *loc. cit.*, p. 372, or 'Scientific Papers,' *loc. cit.*, p. 241.

On the Sequence of Chemical Forms in Stellar Spectra.

By Sir NORMAN LOCKYER, K.C.B., F.R.S.

(Received October 17,—Read November 24, 1910.)

[PLATE 6.]

Introduction.

In the Bakerian Lecture, 1873,* after summarising the observations of stellar spectra and my laboratory researches which had been made up to that time, I wrote: "I have asked myself whether all the above facts cannot be grouped together in a working hypothesis which assumes that in the reversing layers of the sun and stars various degrees of celestial dissociation are at work." The phenomena revealed by the spectroscope seemed to afford a demonstration of the validity of Prout's hypothesis, for so far as the stellar spectra were then known, hydrogen seemed to be the chief constituent of the hottest stars as judged by the extension of the spectrum into the ultra-violet. In a letter to M. Dumas† I wrote: "*Plus une étoile est chaude plus son spectre est simple.*"

The idea that stars with different spectra were entirely composed of different chemical elements gave way to one in which the chemistry was a function of temperature only, the chemistry of all stars having the same basis. I should here state that from the first I have used the term temperature as including electrical effects.‡

In 1888, in another Bakerian Lecture,§ I brought together the various eye observations of the spectra of stars, comets, and nebulae which had been made by others up to that time, and showed that the discussion suggested the hypothesis that all celestial bodies are, or have been, swarms of meteorites, and that the difference between them is one of condensation only. This hypothesis, instead of locating the highest temperature at the commencement of the evolution as demanded by Laplace's hypothesis, placed it much later. Hence bodies of increasing temperature were demanded as well as bodies of decreasing temperature.

In 1892|| I gave an account of the work carried on up to that year in the Solar Physics Observatory on the photographic spectra of stars, and I laid

* 'Phil. Trans.,' vol. 164, Part 2, p. 480 *et seq.*

† 'Comptes Rendus,' 1873, vol. 77, p. 1347.

‡ 'Roy. Soc. Proc.,' 1874, vol. 22, p. 372.

§ 'Roy. Soc. Proc.,' vol. 44, p. 1 *et seq.*

|| 'Phil. Trans.,' vol. 184, pp. 675—726.

before the Royal Society a classification of stars based on the then known chemistry and the extension of the spectra into the ultra-violet so far as it could be determined when glass prisms and lenses were used. I divided the stars into groups and sub-groups, and pointed out that, as more photographs became available, the sub-groups would in all probability become divisible into species.

By 1897 the problem had entered into a new stage. I had in the meantime published the complete spectra of the cleveite gases, including helium, which Ramsay had run to earth,* and by the use of a large coil had discovered a new series of lines, which I termed "enhanced lines," in the spectrum of iron.† By the continuation of this work most of the unknown lines in the spectra of the stars were identified, and stars were found the spectra of which contained the enhanced lines of various metallic elements without the arc lines. The research could therefore be continued on a much wider basis. This was done, and 1897 I laid before the Society a memoir on the chemistry of the hottest stars.‡

At the end of that memoir I wrote: "The above conclusions, based on laboratory, solar, and stellar evidence, all tending in the same direction, may be regarded as the result obtained so far in regard to the 'celestial dissociation' which I pictured to myself in 1873. I claim that each step in the work has demonstrated the truth of that hypothesis more and more, and that we can now acknowledge that the phenomena of the inorganic world are dominated by an evolution not less majestic, although more simple, than that now universally accepted in the case of organic nature."

More recently (1905)§ I have checked the chemical classification by studying the physical condition of stars, using a calcite-quartz optical train to obtain photographs of the extension of the spectra of each chemical group of stars into the ultra-violet on the same plate and under equal conditions of atmosphere and altitude. I found absolute parallelism between the two series of photographs. This, of course, confirmed the prior chemical results.

It is to be remarked that the study of temperature effects in the stars is much more simple and effective than their study in the laboratory, as in the laboratory the effects produced at low temperature are always present, while in the hotter stars, the lowest temperatures where the phenomena observed are produced, may be taken as anything between 5,000° and 20,000° C. There is thus a complete shielding from the effects produced at low temperatures.

* 'Roy. Soc. Proc.' 1895, vols. 58 and 59. several papers.

† 'Roy. Soc. Proc.,' vol. 60, p. 475.

‡ 'Roy. Soc. Proc.,' vol. 61, p. 148.

§ 'Roy. Soc. Proc.,' A, vol. 76, p. 145 *et seq.*

Recent Work on the Classification of Stars.

The more recent researches with better photographs and with increased knowledge of the changes in spectra have enabled me to carry the classification into finer details, and to observe with greater certainty the heat levels at which various chemical forms are predominant. By the term "chemical forms" I mean the molecular grouping, as I termed it 40 years ago (or the corpuscular grouping, as perhaps it may be called now after the recent discoveries of J. J. Thomson, Becquerel, Curie, Ramsay, Rutherford, and others), associated with a special group of lines made visible or more obvious by an increase of temperature in the spectrum of a so-called element *which, in the spectrum of a star, is seen without the low temperature effects* for the reason above stated.

In order to make clear the diagrams in which the new results are shown, we may consider a series of furnaces in the spectra of which, on the dissociation theory, the hottest gives the final result of the simplification brought about by temperature. In each furnace we shall have, as shown by Frankland and myself in 1869,* the chemical form produced in greatest quantity by each temperature indicated by the most widened line, while in the complete spectrum of the mixture of vapours in each furnace the relative thickness of lines will be an indication of the percentage composition† *quâ* the various chemical forms.

The Chemical Forms at Various Heat Levels.

With regard to the spectral lines of the various chemical forms now in question, we have:—

Metals.—Enhanced lines } These are seen separately in stellar spectra.
Arc lines }

Hydrogen.—Pickering's series } These are seen almost separately.
Ordinary series }

Silicium.—Four groups of lines have been made out, some seen separately.

Carbon.—Two groups of lines seen separately.

Sulphur.—Two groups of lines seen separately.

Nitrogen.—Two groups of lines seen separately.

Fig. 1 shows the various heat horizons at which, in the stars, each chemical form is most predominant; I deal only with the series of stars of rising temperatures. The range of each form is also shown. From the furnace analogy we may conclude that at these horizons, owing to the

* 'Roy. Soc. Proc.,' vol. 17, p. 288.

† 'Phil. Trans.,' 1872, vol. 163, p. 639.

heat conditions, each form predominates in turn, owing to a balance between the effects of association and dissociation.

It is most important to observe that in no case is there any break along the line of range, or a double maximum. In this we have most cogent evidence of the continuous working of a law. As we ascend in temperature we find one form giving way to another.

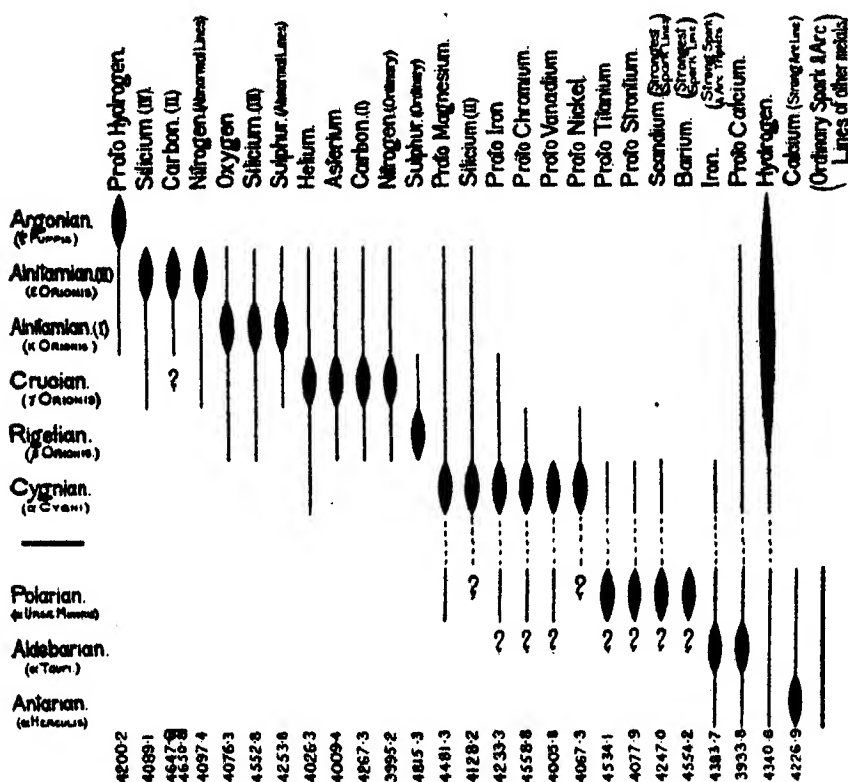


FIG. 1.—Showing the heat levels at which the various chemical forms predominate, and also the range through the stellar groups.

The new results, while entirely in harmony with the old ones, enable us to recognise better than before the stellar demonstration of that celestial dissociation which was first glimpsed in 1873. It must be borne in mind that the record at present is very incomplete. Many of the rarer elements have not yet been studied, the regions in the red and ultra-violet have yet to be explored; only the brighter stars give us spectra which can be discussed in detail.

Special Study of the Alnitamian Stars.

In the classification and catalogue of 470 of the brighter stars published in 1902,* I divided the stars into 16 groups. I had previously stated that sub-divisions must come with better photographs and more knowledge.

The new work has enabled me to make a step in this direction.

Already the Alnitamian stars have been divided into four species. The facts on which this advance is based are shown in fig. 2, in which the various Alnitamian stages are shown in relation to stars higher and lower in temperature, so that the sequence of phenomena may be more completely followed.

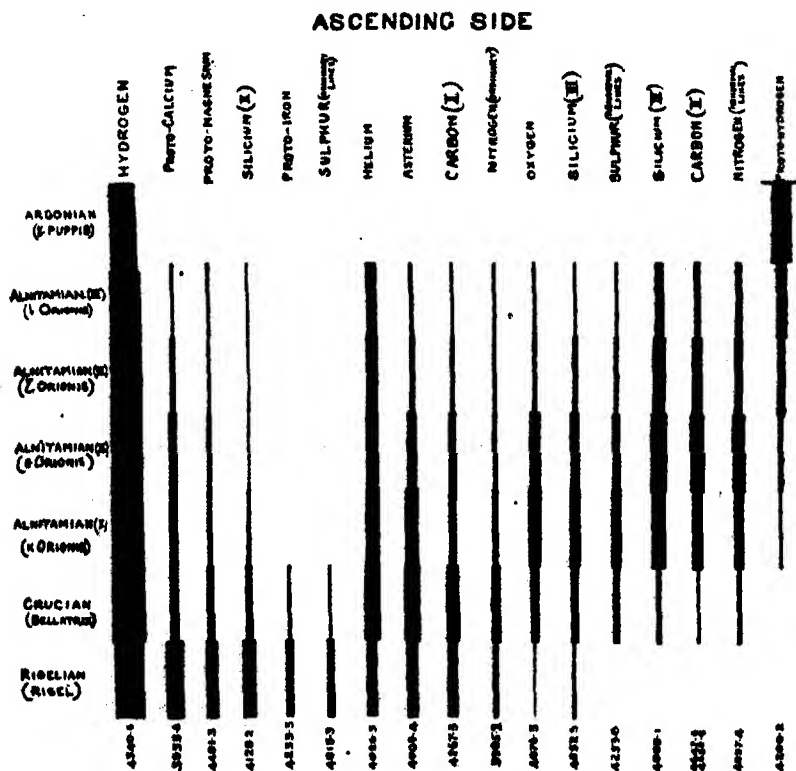


FIG. 2.—Showing the sequence in intensity of typical lines of various chemical forms through the spectra of some of the higher-temperature stars.

Stars with Peculiar Spectra.

The continuation of these researches into the finer details of stellar spectra, in conjunction with laboratory work, is certain to afford help in other directions, notably that dealing with stars showing peculiar spectra.

* Publications of the Solar Physics Committee.

The Henry Draper Memorial researches, under the strenuous direction of Prof. Pickering, have already made us acquainted with a large number of such spectra; unfortunately most of them are of stars so faint as to be beyond the instrumental means at the disposal of the Solar Physics Observatory. They therefore are not included in the catalogue.

But the delicate changes in the spectra of four Alnitamian stars above recorded really provide us with cases of peculiar spectra, and we have now run home the causes of the peculiarities. In ϵ Orionis we have a predominance of silicium IV, in κ Orionis a predominance of oxygen, in ι Orionis a predominance of proto-hydrogen, representing three different temperatures at which these particular chemical forms are produced at the expense of others, which have been driven out of existence by the rise of temperature. The larger the number of chemical forms produced by the dissociation at work, the more numerous must be the minute changes in the spectra if we can only study and record them.

In the Alnitamian stars we are dealing with increasing temperatures.

On the hypothesis put forward in 1888 the stars with rising temperature are much less condensed—are much nearer the nebular stage—than those on the opposite descending arm of the temperature curve; in these latter only can we postulate such a restricted region of absorption as that lying above the photosphere of the sun, which is certainly reducing its temperature and approaching extinction. This view has been strengthened by the recent researches of Prof. Russell, Director of the Princeton Observatory, on the parallaxes, brilliancy, proper motion and spectral types of stars.* He concludes that there ought to be two distinct kinds of red and orange stars greatly differing in condensation, and that "in the intermediate stages the star would be hotter, passing through orange and yellow to white, and back to red as it approaches extinction."

In spite of these different conditions, however, so much are they dominated by temperature that it is temperature and not the other conditions which is effective in producing the spectrum, so similar are the spectra at equal temperatures, whether their temperature is rising or falling, that without the guidance afforded by the different behaviour of the hydrogen lines it would be difficult in the case of the hotter stars to separate the two series. (See Plate 6, fig. 3.)

We have already, in a research on the spectrum of ϵ Ursæ Majoris, found another star with a peculiar spectrum; this star, unlike Alnitam, is cooling.

Its temperature is such that the spectrum of proto-chromium is considerably more developed than in stars of either higher or lower temperature.

* 'Amer. Phil. Soc. Proc.,' 1910, vol. 49, p. 230.

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Other variations from the normal Sirian type in the case of this particular star are the absence of the strong barium line λ 4554.2 and the weakening of the silicium II lines $\begin{cases} 4128.2 \\ 4131.0 \end{cases}$. The strengthening in ϵ Ursæ Majoris of the proto-chromium lines and the absence of the barium line are indicated in Plate 6, fig. 4.

Other Possible Causes of Peculiarity.

In some stars (α Andromedæ, μ Leporis, θ Aurigæ and α Canum Venaticorum) the peculiarity arises from the presence of sets of lines not yet revealed in the laboratory.

The question arises whether some of the other peculiarities may not arise from the fact that we are dealing with close doubles.

Atomic Weights Involved.

I must point out that the chemical forms thus far traced in the stars are associated with the so-called elements having a relatively low atomic weight, and also that, while the evidence for oxygen and nitrogen is now complete, so far the series of atmospheric gases discovered by Ramsay have not been found.

My best thanks are due to Mr. Baxandall, A.R.C.Sc., First Assistant, for the determination of most of the wave-lengths of lines involved in the discussion and for the examination of the photographs. The more recent stellar photographs have been taken by Messrs. Baxandall, Butler, Rolston, Moss, and Goodson. The enlargements for purposes of comparison have been made by Mr. Wilkie.

DESCRIPTION OF PLATE.

FIG. 3.—Showing the variation in thickness of the hydrogen lines and the similarity of the finer lines in stars of about the same heat level, but on different sides of the stellar temperature curve.

FIG. 4.—Comparison of two Sirian spectra (one of normal type, the other peculiar), showing the increased prominence of proto-chromium lines and the absence of the barium line 4554.2 in ϵ Ursæ Majoris (peculiar).

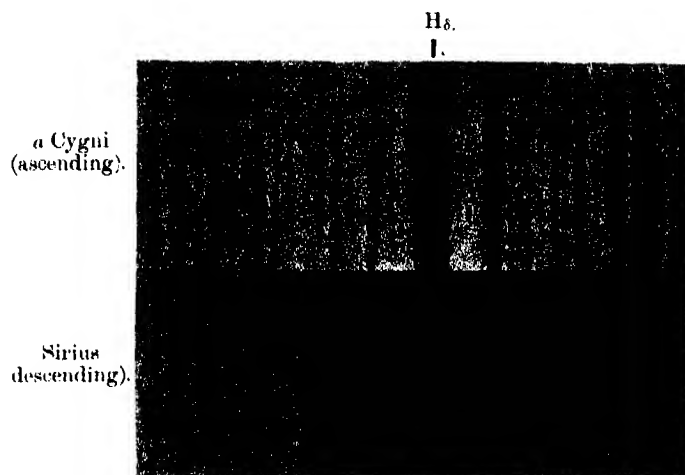


FIG. 3.

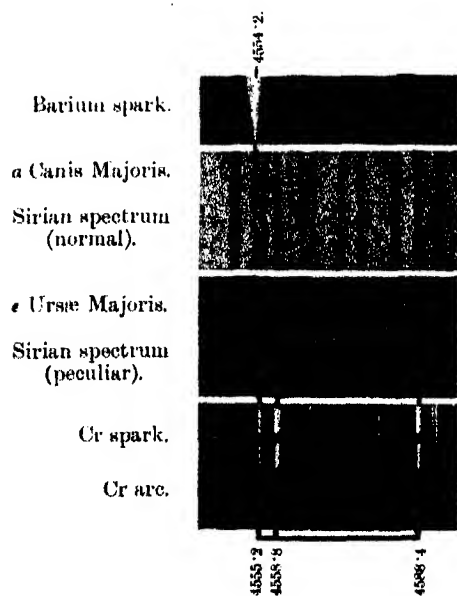


FIG. 4.

A Spectroscopic Investigation of the Nature of the Carriers of Positive Electricity from Heated Aluminium Phosphate.

By FRANK HORTON, M.A., D.Sc., Fellow of St. John's College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S. Received October 24,—Read November 10, 1910.)

The emission of ions from incandescent solids has been studied by many investigators. The value of e/m , the ratio of the charge to the mass, for the carriers of negative electricity was first measured by Sir J. J. Thomson* in the case of a carbon filament heated in a high vacuum. Other observers have since determined the value of this quantity for the negative ions emitted by different incandescent solids, and all agree that the carriers are negatively electrified corpuscles identical in mass from whatever substance they are produced. The investigation of the nature of the carriers of positive electricity emitted by glowing solids presents greater difficulties, owing to the variability of the amount of the positive ionisation produced under different conditions, the causes of which are not yet fully understood. The first measurements of the value of the specific charge of these ions were made by Sir J. J. Thomson,† who found $e/m = 10^4/25$ for the positive ions from a heated iron wire. Later, experimenting with a strip of platinum foil which had already been heated for some hours in a high vacuum, he obtained the value $e/m = 10^4/27$ for the majority of the carriers of positive electricity from that metal. The positive ions thus seem to have the same mass, about 26 times that of the hydrogen atom, in the two cases. This value suggested to Sir J. J. Thomson that they might be molecules of CO or of N₂, either of which has a mass about 28 times that of the hydrogen atom, so that it would be impossible to distinguish between these two gases by a determination of e/m alone. When a luminous discharge was passed through the residual gas in the tube after the experiments with platinum, the band spectrum of carbon monoxide was obtained, and it was concluded that molecules of this gas acted as the carriers of positive electricity from the glowing metal.

Measurements of the value of e/m for the positive ions from platinum and from carbon have been made by a more elaborate method by O. W. Richardson,‡ who finds in the case of these elements values very

* 'Phil. Mag.,' 1899, V, vol. 48, p. 547.

† 'Conduction of Electricity through Gases,' Camb. University Press, 1906, p. 148.

‡ 'Phil. Mag.,' 1908, VI, vol. 16, p. 740.

Note.—In a paper published since this was written Richardson and Hulbirt ('Phil. Mag.,' VI, 1910, vol. 20, p. 245) have found the values of m/H for the positive ions from

nearly the same as those obtained by Sir J. J. Thomson. The values of the ratio of the mass of the carriers to that of an atom of hydrogen given by Richardson's method are—

For platinum $m/H = 25.7$,

For carbon $m/H = 27.6$.

Richardson found that the ions appeared to be quite homogeneous and independent of the temperature of the hot body. He mentions that the values obtained are nearly those required by the molecular weights of nitrogen, oxygen, or carbon monoxide, but he sees no reason for supposing the substances experimented on should give out one or other of these gases. As Richardson states, it is possible that the ions arise from some impurity common to all the materials which have been examined, and he suggests that positively charged sodium atoms would have a value of e/m sufficiently near the values mentioned above. This impurity theory seems difficult to reconcile with the facts that the positive leak from glowing platinum decays with continual heating, but can be restored by exposing the wire to a luminous discharge or by heating it in an atmosphere of any of the commoner gases. On the other hand, if the positive ionisation is caused by an evolution of absorbed gas, it is possible that the passage of a luminous discharge near the wire would lead to reabsorption, or that the same effect would be brought about by heating the wire in an atmosphere of the gas, but one must admit that it is difficult to see why the value of e/m for the positive carriers should be the same whatever gas is used. As a matter of fact, the gas most copiously emitted by a metal when heated is hydrogen, and the values of e/m obtained for the positive carriers make it quite certain that they are not atoms or molecules of that gas.*

The spectrum of carbon monoxide can nearly always be obtained in a vacuum tube when the pressure is very low. Its presence is generally considered as being due to dust in the tube or to grease used in lubricating taps in connection with the apparatus. If a tube gives the CO spectrum, the bands generally obscure the spectrum of any other gas which may

a large number of metals. These values are approximately the same in each case, the mean being 25.3.

* In a paper published after this was written Garrett ('Phil. Mag.,' VI, 1910, vol. 20, p. 582) describes an experiment in which he obtained the value $e/m = 9700$ for "the lightest positive ions present" when aluminium phosphate was heated on a platinum strip in a vacuum. This corresponds with a mass about equal to that of the hydrogen atom. Some hydrogen would be evolved from the heated platinum, and this gas would no doubt be ionised. It would seem, therefore, that Garrett was measuring the specific charge of these ions, which were not detected in Richardson's experiments, and probably form a small proportion of the total ionisation.

be present in small quantity. It therefore seemed desirable to attempt a spectroscopic investigation of the nature of the carriers of positive electricity from incandescent solids, taking the greatest possible precautions to avoid contamination with substances which might give rise to the spectrum of carbon monoxide.

The Method of Experiment.

Certain salts, when heated either in air at atmospheric pressure or in a good vacuum, give a much larger emission of positive ions than is obtained by heating metals or carbon. The behaviour in this respect of a large number of substances was investigated by Sir J. J. Thomson,* and he found that, of the substances experimented on, the greatest effect was given by aluminium phosphate. This salt was therefore used as the source of the positive ions in the experiments which are about to be described.

Some preliminary observations were first of all made to get some idea of the amount of the carriers of positive electricity which might be expected to be set free in an hour from a platinum strip covered with aluminium phosphate and heated in a good vacuum, in order to see if it were likely that they could be detected spectroscopically. With this object in view the current which could be obtained between a platinum strip covered with aluminium phosphate and a surrounding electrode was measured when the strip was at a bright red heat. The quantity of ions required to carry this current was then calculated on the assumption that each ion carried a charge equal to that of a monovalent ion in electrolysis. With a strip of platinum, 25 cm. long and 5 mm. wide, it was found that a current of 10^{-6} amperes could easily be obtained, and by adjusting the temperature of the platinum strip the current could be kept at this value. In one hour this current would liberate, electrolytically, sufficient hydrogen gas to fill a vessel of 1 c.c. capacity at a pressure of 3 mm. of mercury and a temperature of 0° C. If the ions produced from the heated phosphate are monovalent and are capable of existing separately in the uncharged state (unlike the electrolytic hydrogen ions, two of which when discharged combine to form a molecule), the quantity produced by a current of 10^{-6} amperes in one hour would, if confined in the same vessel in the gaseous state, exert twice this pressure at the same temperature. Here we are not assuming that the positive ions from heated substances owe their origin to electrolysis, only that they carry the same charge as the electrolytic hydrogen ion, and the calculation shows that they could be collected in a small vacuum tube at a pressure sufficiently high to allow of a spectroscopic examination of them being made.

* 'Camb. Phil. Soc. Proc.,' 1907, vol. 14, p. 105.

In the actual experiments the small collecting vessel was cooled in liquid air while the current was being passed from the aluminium phosphate to the surrounding electrode. The connection with the rest of the apparatus could then be closed, the liquid air removed, and when the condensed gas had vaporised its spectrum could be examined.

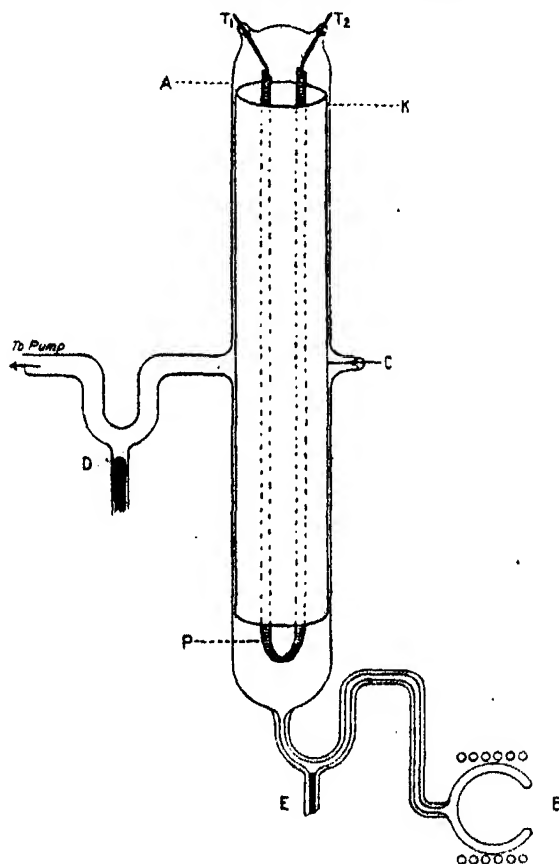
In the earlier experiments a small vacuum tube with aluminium electrodes was used to collect the gases liberated, but the spectrum obtained always contained lines which were thought to be those of gases (chiefly hydrogen) given out by the aluminium electrodes. Small platinum electrodes were next tried, but these too, though better than those of aluminium, were unsatisfactory, and were finally discarded in favour of an electrodeless vessel. A ring discharge in a spherical vessel was used, for it was found to be brighter and more easily worked than the ordinary electrodeless discharge in a straight vacuum tube. In order that the volume of the collecting vessel should not be unduly large it was made by blowing a bulb of about 2 cm. diameter, and then heating the bottom of this and sucking it inside the bulb to within about 1.5 mm. of the outer wall, thus giving a vessel of very small capacity. Preliminary experiments with vessels of this kind showed that with six or eight turns of wire round the bulb a bright ring discharge could be obtained if the gas pressure was between 0.08 mm. and 1 mm. of mercury.

The apparatus used is diagrammatically represented in the figure. The glass used in its manufacture was first of all carefully cleaned with chromic acid to remove grease, and the whole apparatus when completed (but before the platinum strip P was sealed in) was again cleaned out with hot concentrated nitric acid, and afterwards with chromic acid, and finally with distilled water.

The anode P was prepared in the following manner:—A strip of platinum foil, 25 cm. long and 5 mm. wide, was cut, and its ends welded on to thick platinum wire terminals T₁, T₂. The whole was then boiled for some hours in concentrated nitric acid to clean it and to remove hydrogen. It was then washed with distilled water, suspended in a clean tube, and heated by an electric current to bright redness for about an hour. It was covered with a uniform layer of aluminium phosphate by making a thin paste of the latter with distilled water, dipping the strip into this paste, and then warming it gently by means of the electric current until quite dry. This process was repeated several times until the strip was completely covered with aluminium phosphate. It was then sealed into the apparatus.

In the diagram K is a thin sheet of platinum foil bent into a tube of slightly smaller diameter than the glass tube A (about 2.5 cm.) and joined

to the platinum wire C for connection to a battery of accumulator cells. The aluminium phosphate covered strip, P, hangs inside the platinum tube without touching it, and the current between the strip and the tube can be measured by means of a d'Arsonval galvanometer. The connection to the mercury pump, McLeod gauge, drying tubes, and carbon tube for producing a very low vacuum by cooling in liquid air is shown in the figure. This



connection could be broken by raising the mercury in the cistern of the barometer tube D.

B is the bulb for collecting any substance evolved during the passage of the discharge in the tube A. This bulb was about 2 cm. in external diameter, and the distance between the two walls was about 1.5 mm. It was connected by capillary tubing to the discharge tube A, the connecting tubing being as short as possible. This connection could be cut off by means of the mercury column E. The bulb B could be surrounded by liquid air for the purpose of condensing any evolved gases which could be liquefied by

cooling to that temperature. A small coil of six turns of insulated flexible wire, such as is used for electric lamps, was made to fit the bulb. It could be slipped over B with its axis in the plane of the paper as indicated in the figure. The ends of the coil were connected to the outside coatings of two large Leyden jars, the inside coatings of which were connected to an induction coil with an electric valve in series. An adjustable spark gap was arranged between the two inside coatings, and as sparks passed across this gap they were accompanied by a ring discharge in the bulb B. The spectrum of the discharge was viewed by means of a Hilger direct wave-length spectroscop.

The apparatus was evacuated by means of a mercury pump, and was then left for some time to make sure there was no leakage anywhere. The conditions under which the ring discharge could best be obtained were then investigated, experiments being made at different low pressures and with varying lengths of air gap between the sparking knobs. It was found that the ring discharge was at its best when the pressure in the bulb was between 0.1 mm. and 0.5 mm., although it could sometimes be obtained with the pressure as low as 0.03 mm. This seemed very satisfactory, and showed a distinct advantage over the ordinary vacuum tube arrangement, in which, at these low pressures, the luminosity of the discharge is very faint. The spectrum of the ring discharge through the residual gas in the apparatus was carefully observed. It was found to be the elementary line spectrum of air, consisting of a large number of nitrogen lines with some lines of oxygen and the hydrogen red line. Five or six lines of the mercury spectrum were also present.

The gas pressure in the apparatus was then reduced as low as possible by means of charcoal cooled in liquid air, and the tube A was then cut off from the pump and charcoal tube by raising the level of the mercury cistern in connection with the barometer D. The temperature of the platinum strip P was raised to over 1000° C. by connecting its terminals to the town alternating current supply through a set of resistances which could be varied so as to adjust the current to give the required temperature in the strip. The bulb B was immersed in liquid air to condense anything liquefiable at that temperature which was given off by the heated strip. After about two hours the heating current was cut off, the connection at E was closed, and the liquid air was removed. Gas to a pressure of about 5 mm. developed in the bulb B, and, as this pressure was too great to give the electrodeless ring discharge, it was lessened by reopening the connection at E and allowing some of the gas to escape into the main tube A. The ring discharge was then easily obtained and its spectrum showed many of the brightest nitrogen

lines, also the hydrogen red line very brightly and several of the mercury lines. A few lines of carbon were also measured, the double red line λ 6584, 6579 being particularly brilliant.

The existence of nitrogen lines in this spectrum was taken as showing that all the air had not yet been got rid of. It is probable that the warming up of the glass apparatus during the heating of the strip had driven off some of the air which is known to cling to the walls of an exhausted tube, and that it was this which was producing the nitrogen lines in the spectrum. The hydrogen line was probably from gas evolved by the heated platinum strip.

Before the experiment proper could be performed it was obviously necessary to get rid of this liberation of gas on merely warming the glass apparatus. The connection to the pump, etc., was again opened and the whole apparatus was again evacuated by means of the charcoal tube cooled in liquid air. The above experiment was then repeated and the spectrum of the condensed gas again observed. The nitrogen lines were now much fainter, and on repeating the evacuation and heating several times they completely disappeared. It was found that the amount of gas collected while the platinum strip was maintained at a high temperature became gradually less, but although the heating was repeated some 8 or 10 times, on each occasion for about two hours, it was found that some gas could always be collected. The lines measured in the spectrum of this gas are given in the first column of the table on p. 440. When all the air had been got rid of, the effect of having a measured current passing from the heated aluminium phosphate to the surrounding cylinder was investigated. The platinum strip covered with aluminium phosphate was earthed. The positive terminal of a battery of small accumulator cells was also earthed, and the negative terminal was insulated and connected through a d'Arsonval galvanometer to the platinum cylinder surrounding the strip. The vacuum having been made as good as possible, the apparatus was isolated from the pump and the platinum strip was raised to a temperature of about 1000° C. A difference of potential of 120 volts was then established between the earth-connected end of the strip and the cylinder. The bulb B was surrounded with liquid air and the discharge allowed to go on for about two hours. During this time the galvanometer deflections were read at intervals of about a quarter of an hour. The deflections were not steady, but tended to decrease. This was prevented by gradually increasing the temperature of the platinum strip. The mean of the galvanometer deflections corresponded to a current of 8.4×10^{-6} amperes, a current sufficient to liberate by electrolysis 2.5 c.c. of hydrogen gas per hour, measured at 0° C. and at a pressure of 1 mm. of mercury.

At the conclusion of this run the bulb B was separated by the mercury cut-off from the rest of the apparatus, and the spectrum of the ring discharge in the collected gas was examined. It was found to consist of practically the same lines as the spectrum of the gas collected by simply heating the aluminium phosphate without the negative potential being applied to the surrounding cylinder. The lines measured, together with their intensities, are recorded in the following table. Most of them have been identified as being due to carbon, oxygen, hydrogen, or mercury:—

Lines measured in the spectrum of the gas collected after the sixth heating of platinum strip covered with aluminium phosphate.	Intensity.	Lines measured in the spectrum of the gas collected after current of 8.4×10^{-3} amperes had passed for 2 hours between heated aluminium phosphate and surrounding electrode.	Intensity.	Lines identified as λ .
6582	8	6582	10	{ 6584 } C
6563	10	6563	10	{ 6579 } H
6152	1 b	6152	1—5	6563 H
6096	8	6097	8	6152 Hg
5890	10	5890	10	5889 Hg
		5878	1	
5791	1	5791	1—4	5791 Hg
5771	1	5771	1—4	5770 Hg
5696	5	5696	4	
5679	4	5679	5	5679 Hg
5663	2	5663	2	5662 C
5649	2	5649	1	5649 C
5640	1	5640	1	5641 C
5460	2—10	5460	10	5461 Hg
5427	3	5427	2	5427 Hg
5206	3	5206	2	5207 O
5152	2	5152	2	5152 C
5146	8	5146	5	5145 C
5138	6	5138	5	5138 C
4940	3	4940	3	
4924	2	4924	2	4925 O
4907	2	4907	2	4907 O
4891	1	4891	1	4892 O
		4850	5	
4700	4 b	4700	3 d	{ 4706 } O
		4675	1 p	{ 4700 } O
		4660	1 p	4676 O
4650	8 b	4648	8	4662 O
4641	3 b	4640	3 b	4640 O
4593	3 b	4593	2 d	{ 4642 } O
				{ 4639 } O
4416	3 b	4418	4	{ 4597 } O
		4357	4	{ 4591 } O
4350	1 b	4352	2	{ 4417 } O
4270	6 b	4270	2	{ 4415 } O
				4359 Hg
				{ 4352 } O
				{ 4349 } O
				4267 C

b signifies that the line was blurred, not sharp.

d signifies that the line was thought to be a double one.

The wave-lengths in the last column were taken from Kayser's 'Handbuch der Spectroscopie,' those of mercury lines being from the observations of Eder and Valenta, the carbon lines by Gramont, and the oxygen lines by Neovius.

On first taking away the liquid air the pressure in the bulb B was too low for the ring discharge to pass. This began as the bulb warmed up, and it was noticed that the mercury lines were the last to appear in the spectrum. These always brightened up considerably as the tube was worked, owing to the increasing vapour pressure of the mercury which had been condensed in B during the first part of the experiment.

It was found that the brilliance of the ring discharge could be considerably reduced by surrounding the bulb B with iced water to keep it cool. In the spectrum, under these conditions, the lines marked as mercury were all greatly diminished in brightness, most of the weaker ones disappearing. The unidentified lines also disappeared, except λ 4940, which became very faint. The carbon, oxygen, and hydrogen lines remained, but were of slightly diminished intensity.

It has been stated that, in the first experiments which were made, instead of using the ring discharge to test the spectrum of the gas collected, a small vacuum tube of the ordinary kind was employed. In these experiments the spectrum obtained showed the hydrogen red and blue lines and some of the brighter lines of the secondary hydrogen spectrum, together with the band spectrum of carbon monoxide. The hydrogen lines became brighter as the vacuum tube was worked, which seemed to suggest that this gas was coming out of the electrodes. It was for this reason that the tube was discarded and the electrodeless bulb used. From the table it appears that the oxycarbon spectrum was not due to the metallic electrodes, for the lines of carbon and of oxygen point to the presence of an oxide of carbon in the gas collected. In order to see if this supposition were correct, the apparatus shown in the figure was modified by putting a small vacuum tube of the ordinary shape, but without electrodes, in connection with the bulb B. The small tube had its ends covered with tinfoil, which was bound on by insulating tape and then waxed over. On repeating the experiment and observing the spectrum of the gas collected in the two tubes, it was found that whereas the ring discharge gave the lines of carbon and oxygen, the ordinary electrodeless discharge gave the band spectrum usually attributed to carbon monoxide. It is probable that this difference is due to the decomposition of the carbon monoxide by the ring discharge. This is similar to the result obtained with air. It has been mentioned that the spectrum of the ring

discharge through the residual air in the apparatus, before the platinum strip had been heated, was the "elementary line spectrum" of air, whereas the spectrum obtained from air at a low pressure in an ordinary vacuum tube is a series of bands due to nitrogen. The difference between the two spectra is probably due to the dissociation of the nitrogen molecules at the higher temperature of the ring discharge. The ring discharge is an oscillatory discharge from Leyden jars, and the production of line spectra under these conditions is in accordance with the general rule that increasing the amount of energy in the discharge by the introduction of capacity into the circuit has the effect of increasing the number of lines in the spectrum obtained. This increase is usually greatest at the blue end of the spectrum, as, for instance, in the case of argon. In the present case of carbon monoxide I was unable to change the band spectrum of the ordinary electrodeless discharge into the line spectra of carbon and oxygen by placing a Leyden jar and spark gap in parallel with the tube, although Smithells* has found that with a vacuum tube with electrodes, at low gas pressures, this change takes place as the spark gap is gradually widened. The difficulty of sending a heavy discharge through the electrodeless tube probably accounts for this change not occurring in these experiments.

It might here be mentioned that the difference between the spectrum of the ring discharge and the ordinary vacuum tube spectrum of carbon monoxide is in agreement with the theory of Sir J. J. Thomson as to the origin of line spectra and band spectra. According to this theory, banded spectra are due to the vibrations of electrical doublets, each consisting of a negatively charged particle bound to a positively charged particle inside the atom or molecule, whereas line spectra are produced by the vibrations of small negatively charged corpuscles outside the atom. It does not seem improbable that the extra energy of the ring discharge should lead to a splitting up of the electrical doublets inside the CO molecule, liberating electrons which, by their vibrations, give rise to the lines obtained in the spectrum of the ring discharge.

The fact that the gas collected when a continuous current is passing from the heated aluminium phosphate to the surrounding cylinder gives the same spectrum as the gas obtained when no external E.M.F. is applied, might be taken as indicating that the positive ions have escaped collection, or that they are present in such small quantity as not to produce any change in the spectrum observed, were it not that we have already seen that the total quantity of electricity carried by these ions

* 'Phil. Mag.,' 1901, VI, vol. 1, p. 476.

during the experiment is so great that it might reasonably be expected that they are produced in sufficient quantity to be detected by the spectro-scope. We must take it that the positive ions are present in the collected gas in sufficient quantity for their spectrum to be observed, and I think these experiments show that they consist of molecules of carbon monoxide or of oxygen. Although no oxygen lines were visible in the ordinary vacuum tube discharge through the collected gas, it must be remembered that these lines do not show up when oxygen is mixed with nitrogen, and they would probably also be obscured by the presence of carbon monoxide. We cannot, therefore, be sure that the oxygen lines obtained in the spectrum of the ring discharge are entirely due to the effect of that discharge on the carbon monoxide gas, although this would be a satisfactory explanation of their presence. On the other hand, the carbon lines in the spectrum of the ring discharge are probably due entirely to the carbon monoxide, for carbon in the gaseous condition could only be present in the bulb at the instant of dissociation of that gas. In this connection it should be mentioned that there was no noticeable deposition of carbon in the bulb, so that the dissociation into carbon and oxygen must have been followed by a complete recombination of these elements when the ring discharge was stopped.

Carbon monoxide and oxygen are two of the gases mentioned by Richardson as possible carriers of the positive charges from the point of view of their molecular masses. The entire absence of nitrogen lines from the spectrum of the gas collected in these experiments seems to preclude the possibility of the positive ions consisting of nitrogen. If they do consist of an elementary substance, it would be more in accordance with the nature of positive ions from other sources if they are atoms and not molecules.

In ordinary electrolysis we have the atoms of elementary substances acting as the carriers of the electric charges, but in certain cases we have also compound radicals, consisting of groups of atoms, acting as the carriers of the positive charge. There seems to be no reason why, in the case of the discharge of electricity from a glowing solid, the positive ion should not consist of CO, a compound radical acting like an atom, for we know that this group plays the part of an atom in many chemical reactions.

Five of the lines recorded in the table on p. 440 are there not attributed to any element. It may be that these, together with other lines only faintly visible and not measured in these experiments, form the spectrum of the carriers of positive electricity from heated aluminium phosphate, but I am inclined to think that they are due to some other cause. Each of the lines 6097, 5878, 5696, 4940, 4850, corresponds to a line in the secondary spectrum of hydrogen, but the corresponding secondary hydrogen lines are

very faint, except in the case of 4849, which is of intensity 4. In my experiments the line 4850 was only observed in one set of experiments. The other four lines were always seen, and I am inclined to attribute their presence to mercury, although they are not lines which are usually seen in the mercury spectrum. Like most of the mercury lines observed in these experiments, they increased in brightness as the tube warmed up with continual working, and like all the fainter mercury lines, they disappeared when the bulb was kept cool in iced water while the spectrum of the discharge was being observed.

Some time ago the writer* drew attention to five lines in the red and orange regions of the mercury spectrum which, though generally invisible, were obtained very brightly when a luminous discharge from a glowing lime-covered cathode is produced in mercury vapour. Since then the spectrum of mercury has been more closely studied, and it has been found that when the ordinary vacuum tube discharge, with capacity in parallel, is taken in mercury vapour at a very low pressure, a large number of new lines come into prominence. These lines (and the red and orange lines referred to above) may not be due to mercury vapour in a normal condition, but may be produced by something formed from mercury by the passage of the electric discharge through its vapour—some new arrangement of corpuscles which again becomes mercury when the discharge ceases. Two experiments which have recently been made seem to support this view. The first of these is an experiment described by Dr. H. Brereton Baker at a recent lecture at the Royal Institution.† If oxygen is allowed to enter a mercury lamp immediately after the current has been cut off, it is found that a considerable quantity of mercuric oxide is formed, although the temperature is much lower than that at which mercury vapour in a normal condition combines with oxygen. Evidently the ionised mercury vapour remaining in the lamp has different chemical properties from mercury vapour in the ordinary atomic condition, and the spectrum given by this vapour may depend upon the nature and extent of the ionisation. This view is also supported by the recent experiments of Ladenburg on the absorption spectrum of hydrogen. Ladenburg found that when light from a hydrogen vacuum tube was sent through a long tube containing hydrogen gas, no absorption took place unless the gas in the long tube was also conveying an electric current, in which case marked absorption of the hydrogen red light was obtained. It looks, therefore, as though the hydrogen red line were given out by some arrangement of corpuscles not

* 'Camb. Phil. Soc. Proc.' 1908, vol. 14, p. 501.

† See 'Nature,' 1910, vol. 84, p. 388.

present in hydrogen in the ordinary condition, but manufactured from the gas by the passage of the electric current. In the case of mercury we have a vapour of high atomic weight, and one which is very easily ionised, and it would seem that new corpuscular arrangements might be formed more readily than in the case of hydrogen. That the brightness of different lines given by mercury vapour varies enormously under different conditions is well illustrated by the intensities given in the table on p. 440 by the brightness of the yellow line $\lambda 5889$ in the spectrum of the electrodeless ring discharge, at a time when the two yellow lines $\lambda 5770$ and $\lambda 5791$, usually so prominent in the mercury spectrum, were only faintly visible.

I think it is probable, therefore, that the lines $\lambda 6097$, 5878 , 5696 , and 4940 are due to the passage of the electrodeless ring discharge through the mercury vapour present in the discharge tube.

Conclusion.

It has been pointed out that from the magnitude of the total quantity of electricity carried from the heated aluminium phosphate to the surrounding electrode we are justified in assuming that the positive ions are set free in sufficient numbers for their spectrum to be observed. The spectroscopic evidence shows that carbon monoxide, hydrogen, mercury vapour, and possibly oxygen are present in the apparatus, all of these, with the exception of mercury, being liberated by the heating of the platinum strip covered with aluminium phosphate. The values of e/m for the carriers of positive electricity obtained by Richardson make it certain that these carriers cannot be atoms or molecules of hydrogen or mercury; and in this paper reasons have been given for thinking it doubtful whether oxygen is really present in the free state in the tube. Richardson's values of e/m make the mass of the carriers considerably greater than that of the oxygen atom, and I think it is more likely that the ions, if they consist of an elementary substance, are atoms, not molecules. The fact, too, that oxygen is strongly electro-negative in character would seem to be against its acting as a carrier of positive electricity.

The conclusion arrived at is, therefore, that the positive ions are molecules of carbon monoxide. The mass of these molecules is very near to that required to fit in with the value of the specific charge obtained for the positive ions from iron, platinum, and carbon. We are assuming that the carriers of positive electricity are the same in the case of aluminium phosphate, an assumption which seems to be justified by the experiments of Brown,* who has shown that the kinetic energy of these ions is the same as that of the ions from metals.

* 'Phil. Mag.,' VI, 1909, vol. 18, p. 649.

The question arises, is this carbon monoxide evolved from the heated aluminium phosphate, or is it produced from the glass walls of the apparatus? In the experiments which have been made to determine the value of the specific charge and the kinetic energy of the carriers of positive electricity from heated substances, there can be no doubt that relatively large amounts of carbon monoxide were present in the apparatus used. In the experiments described in the present paper the utmost care was taken to have the whole apparatus free from traces of dust or grease or anything which might give rise to carbon monoxide gas. With glass cleaned in the same way as the apparatus used in these experiments, the writer has had vacuum tubes containing mercury heated so that the spectrum of the electric discharge through the vapour might be observed, and only after long continued heating has the spectrum of carbon monoxide appeared. In the case of these mercury vacuum tubes the inner surface of the glass became broken up by continued sparking from the surface of the mercury while the discharge was passing, and this might be expected to allow any gas occluded or dissolved in the glass to escape into the vacuum tube, and probably accounted for the CO spectrum which was sometimes seen in tubes that had been worked for several weeks. In the present experiments no such breaking up of the glass surface occurs, and it would be much more difficult for gas to escape into the tube from inside the glass. The gas occluded on the surface would be got rid of during the first few heatings and evacuations.

It must, however, be mentioned that the experiment was tried of heating up the glass by means of a Bunsen burner while the aluminium phosphate remained cold, and it was found that a small amount of gas could be collected in the bulb cooled in liquid air and this gas gave the carbon monoxide spectrum, but the amount of gas collected in this way was not nearly so much as when the aluminium phosphate was heated. In heating the apparatus from outside with the Bunsen flame parts of the glass were no doubt made much hotter than when heated by the radiation from the glowing platinum strip, and gas occluded on these parts might thus have been removed.

It would be much easier to imagine that the CO spectrum is due to the heating of the glass than that it is evolved from the aluminium phosphate, for the carbonates used in the manufacture of glass might be expected to evolve CO_2 which in a vacuum tube gives the same spectrum as CO, the reason for this being, according to Liveing* that the carbonic acid gas dissociates into carbon monoxide and oxygen and the former acts as the carrier of positive electricity through the tube. I tried to estimate whether more gas was produced in the apparatus when a current was passing from the heated

* 'Camb. Phil. Soc. Proc.', 1904, vol. 12, p. 338.

strip to the surrounding electrode than when the latter was insulated, but I was unable to come to any definite conclusion. The experiment could easily be performed by having a small McLeod gauge in immediate connection with the discharge tube A or the condensing bulb B. In these experiments, however, the apparatus was designed to have as little surface of glass as possible, in order to avoid trouble from the occluded gas.

Reference has already been made to the fact that the spectrum of the gas collected is the same whether it is obtained when the aluminium phosphate is heated without an external electric field being applied from the battery of cells, or with a current passing from the strip to the surrounding electrode. In the first case it might be thought that no ions would be set free, but the liberation would still go on for a short time. Sir J. J. Thomson found that aluminium phosphate evolves positive ions when heated without the application of any electric field, and it must be remembered that in the present experiments the phosphate was heated by an alternating current, which would cause it alternately to drive out and to draw back positive ions. If the surrounding cylinder is so near to the heated strip that the positive ions reach it before the potential difference between the electrodes is reversed, they would give up their charges to the cylinder and be set free in an uncharged condition. Other ions emitted by the heated phosphate would, no doubt, discharge themselves to the sides of the glass tube, and, perhaps, to the mercury in the adjacent barometer tube. That positive ions were shot off in this way and charged up the surrounding platinum cylinder was proved by connecting this to earth through the galvanometer. On heating up the phosphate by the alternating current a large deflection was obtained, the current passing across the tube being about the same as when the saturation E.M.F. was applied from the cells.

When the electrode surrounding the platinum strip is insulated, as in the experiment from which was obtained the spectrum recorded in the first column of the table on p. 440, the ions would cease to be emitted from the heated strip after the surrounding electrode had become charged to a certain potential, depending upon the maximum positive potential attained in the strip. As already stated, experiments made to see whether more gas was evolved while the current was passing across the tube than when the cylindrical electrode was insulated led to no definite result, but the fact that the gas collected in each case gave the same spectrum may, perhaps, be due to ions being condensed in both experiments, although the number collected would be very much greater while the current was running than when the cylinder was insulated. If carbon monoxide gas is evolved from the heated aluminium phosphate, and if it is molecules of this evolved

gas which act as the positive ions, it would follow that much more gas is evolved while the current is passing from the heated electrode than when the surrounding cylinder is insulated, or else that a larger percentage of the molecules of the evolved gas is ionised when the heated phosphate is at a higher positive potential than the surrounding cylinder than when this is not the case.

That carbon monoxide should be evolved from metals and from aluminium phosphate when heated seems very mysterious. It is well known that many metals, notably platinum and palladium, evolve hydrogen when strongly heated, but the presence of this elementary gas can be more readily accounted for than could the presence of a compound like carbon monoxide.

I believe that, for some unknown reason, the aluminium phosphate used in these experiments did evolve some (at least) of the gas which gave the carbon monoxide spectrum, but it is difficult to believe that this gas is also emitted by all the materials heated in the kinetic energy experiments of Brown. However, there can be no doubt that carbon monoxide was present in the apparatus used by Brown, and even if it were not in the first place evolved by the substances experimented on, I think it may still have acted as the positive ion as indicated by the uniformity of the results obtained.

No doubt the molecules of carbon monoxide would more readily act as carriers of positive electricity from a substance if they came from inside that substance than if they only got in contact with its surface. Now carbon monoxide has the property of readily diffusing into carbon and into a number of metals; it is also not easily dissociated by heat or by the electric discharge.* When a metal is heated in an atmosphere of carbon monoxide, molecules of the gas would be continually entering and leaving the surface of the metal. Many of those leaving would, as a rule, be ionised and carry away a positive charge, but this leakage of positive electricity could be prevented by an opposing E.M.F., which would cause the molecules escaping with a positive charge to diffuse back again into the metal.

The question arises, why does this not happen to other gases when present in the apparatus? I should have expected it would happen to some extent; especially in the case of a strongly electro-positive gas such as hydrogen; but hydrogen would be present in the molecular condition, and ions usually consist of atoms when an elementary substance is concerned. The CO radicle, though compound, acts as an atom in many chemical combinations. It would appear also to have a greater affinity for positive electricity than

* J. N. Collie, 'Chem. Soc. Journ.,' 1901, vol. 79, p. 1063.

any of the ordinary gases, as is evidenced by the readiness with which the spectrum of carbon monoxide shows up in vacuum tubes, often to the total exclusion of the spectrum of other gases which are known to be present.

If the view that the positive ions from heated substances are molecules of carbon monoxide is correct, it would mean that a substance which of itself evolved this gas when heated would probably have a greater positive leak than one which did not do so. A large emission of positive ions would also be expected to be obtained from a substance which had a strong affinity for negative electricity, and would thus more readily allow the molecules of gas to escape with a positive charge. This is probably a property of phosphorus at high temperatures, for Sir J. J. Thomson has shown that the phosphates as a class emit large amounts of positive electricity when heated.

The author wishes to take this opportunity of thanking Prof. Sir J. J. Thomson for his interest in these experiments, which were carried out in the Cavendish Laboratory, Cambridge.

Colour-Blindness and the Trichromatic Theory of Colour Vision.
Part II.—Incomplete Red or Green Blindness.

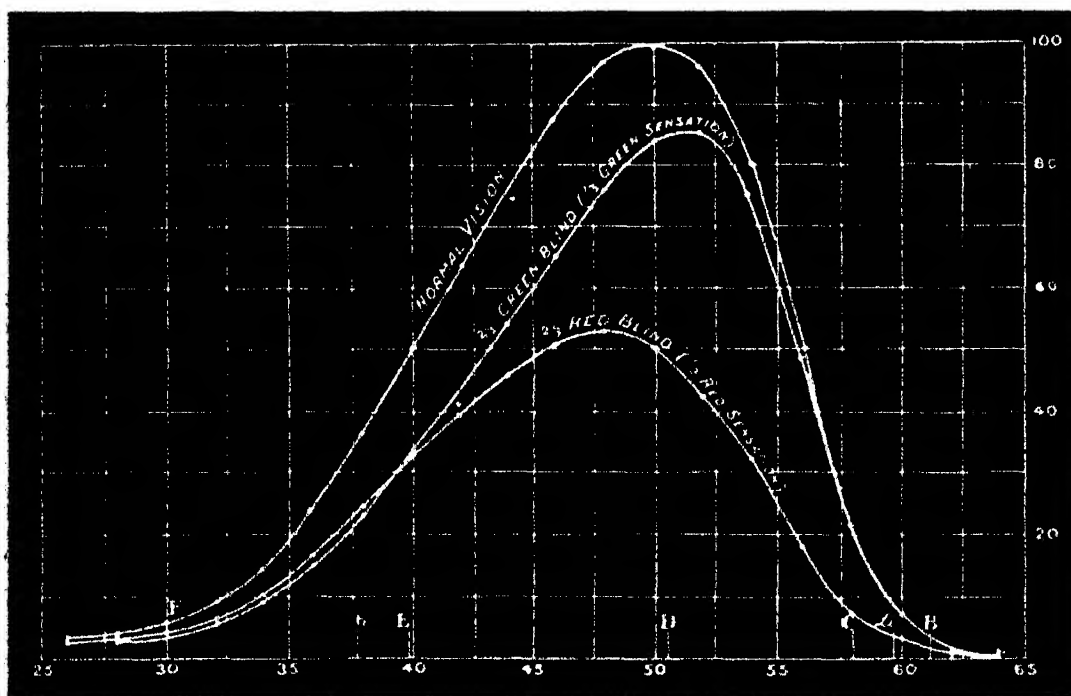
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In Part I of this subject* I treated of complete colour-blindness in its relation to the trichromatic theory of colour vision. In this communication, which is a continuation of that published, I deal with incomplete colour-blindness and its relation to the same theory. The number of cases of incomplete red or green blindness is larger than those where the colour-blindness is complete. In cases of incomplete colour-blindness so far as they have come under my examination the sensation curves of the red and green sensations are similar (in a mathematical sense) to those existing in normal vision, that is to say, if in the normal (say) red curve an ordinate of one colour indicates a perception of "a" red, and for the incomplete red-blind a perception of "b" red, then in any other position in the spectrum the proportion of normal to incomplete red-blindness is as $a:b$. This

* 'Roy. Soc. Proc.,' A, 1910, vol. 83.

fact leads to a far-reaching conclusion. It tells us that the place of maximum luminosity travels in the case of red-blindness from Standard Scale No. (S.S.N.) 50 to S.S.N. 46. A reference to Table I will show why such travelling of maximum luminosity takes place. To take two examples, a table (Table II) and diagram of luminosity curves for eyes which only perceive one-third of the red sensation and one-third of the green sensation is given. In the first the maximum is closely at S.S.N. 48 (λ 5720), and in the second at S.S.N. 51 (λ 5922). The maximum at S.S.N. 49 (λ 5873) is when the red sensation is about two-thirds of the normal, and at



S.S.N. (47) (λ 5658) when it is about one-tenth of the normal, at S.S.N. 46 (λ 5600) when there is no red sensation. In the green-blind when there is no green sensation the maximum is closely at S.S.N. 52 (λ 6000).*

By observing the position of maximum luminosity we can form an approximate diagnosis of the amount of the defect and as to the sensation in which the defect exists.

Suppose that we have a luminosity curve taken by (say) an incompletely

* In this communication as in the last the white light which forms the spectrum is from the crater of the positive pole of the arc light. If any other source of light be used the maxima will not be in the same positions as those given.

red-blind eye the question comes whether we can find the exact amount of deficiency that exists or, at all events, approximate to exactness.

If by any means we can make the ordinates of the curve obtained of proper height when compared with those of the normal vision curve (which

Table I.—Showing the Composition of the different Rays of the Spectrum in Terms of Luminosity of the Three Sensations.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Standard scale number (S.S.N.)	λ .	Luminosity of spectrum.	Percentage composition of colours in terms of sensations.			Luminosity of sensation.		
			R.S.	G.S.	B.S.	R.S.	G.S.	B.S.
64	7217	0.5	100	—	—	0.5	—	—
62	6957	2	100	—	—	2	—	—
60	6728	7	100	—	—	7	—	—
58	6521	21	99	1	—	20.79	0.21	—
56	6330	50	95.5	4.5	—	47.75	2.25	—
54	6152	80	90.5	9.5	—	72.40	7.60	—
52	5996	96	84.2	15.8	—	80.64	15.36	—
50	5850	100	75	25	—	75	25	—
48	5720	97	67.12	32.9	0.080	65.16	31.78	0.029
46	5596	87	62.3	37.60	0.104	54.20	32.70	0.080
44	5481	75	58.1	41.74	0.158	48.57	31.30	0.118
42	5373	62.5	55.4	44.4	0.196	34.61	27.75	0.122
40	5270	50	51.57	48.20	0.224	25.60	24.09	0.112
38	5172	36	48.65	51.1	0.252	17.50	18.43	0.091
36	5065	24	46.08	53.5	0.420	11.09	12.83	0.101
34	5002	14.2	43.79	55.34	0.670	6.22	7.86	0.124
32	4924	8.5	42.17	56.13	1.700	3.58	4.77	0.145
30	4848	5.7	42.24	54.60	3.160	2.45	3.08	0.174
28	4776	4	44.26	50.54	5.200	1.76	2.03	0.202
26	4707	2.8	50.02	41.30	8.680	1.41	1.15	0.243
24	4639	1.95	58.56	28	18.44	1.15	0.53	0.262
22	4578	1.4	65.56	16.8	17.64	0.61	0.27	0.247
20	4517	1.1	70.72	8	21.28	0.77	0.10	0.234
18	4459	0.86	71.88	4.6	23.52	0.62	0.04	0.202
16	4404	0.70	72	2	25.76	0.51	0.01	0.180
14	4349	0.56	72	0.5	27.44	0.392	—	0.154
12	4296	0.45	72	—	28	0.384	—	0.126
10	4245	0.35	72	—	28	0.258	—	0.098
8	4198	0.26	72	—	28	0.187	—	0.073
6	4151	0.18	72	—	28	0.180	—	0.051
4	4106	0.14	72	—	28	0.101	—	0.039
2	4062	0.10	72	—	28	0.076	—	0.028
0	4010	0.06	72	—	28	0.057	—	0.022

A is 67.2; B, 61.3; Red lithium, 59.8; C, 58.1; D, 50.6; E, 39.8; δ , 37.7; F, 30.0; Blue lithium, 22.8; G, 11.2; H, — 7.1.

Table II.—Showing incomplete Red and Green Blindness.

S.S.N.	λ.	Normal lumi- nosity.	Red-blind.				Green-blind.			
			Lumi- nosity of red- blind.	‡ R.S.	G.S.	B.S.	Lumi- nosity of green- blind.	R.S.	‡ G.S.	B.S.
64	7217	0.5	0.2	0.2	—	—	0.5	0.5	—	—
62	6957	2	0.66	0.66	—	—	2.0	2.0	—	—
60	6728	7	2.33	2.33	—	—	7.0	7.0	—	—
58	6521	21	7.14	6.98	0.21	—	20.9	20.8	0.7	—
56	6380	50	18.1	15.9	2.25	—	48.6	47.8	0.75	—
54	6152	80	31.7	24.1	7.60	—	74.9	72.4	2.5	—
52	5996	96	42.8	26.9	15.40	—	85.8	80.6	5.2	—
50	5850	100	50.0	25.0	25.00	—	88.3	75	8.3	—
48	5720	97	53.5	21.7	31.8	0.08	75.9	65.2	10.6	0.08
46	5596	87	50.9	18.1	32.7	0.10	65.0	54.2	10.7	0.10
44	5481	75	45.9	14.5	31.3	0.12	54.1	43.6	10.4	0.12
42	5378	62.5	39.3	11.5	27.7	0.12	40.9	31.6	9.2	0.12
40	5270	50	32.8	8.6	24.1	0.11	38.9	25.8	8.0	0.11
38	5172	36	24.3	5.8	16.4	0.09	28.7	17.5	6.1	0.09
36	5085	24	16.6	3.7	12.8	0.10	15.5	11.1	4.3	0.10
34	5002	14.2	10.0	2.1	7.8	0.12	8.9	6.2	2.6	0.12
32	4924	8.5	6.1	1.2	4.8	0.14	5.3	3.6	1.6	0.14
30	4848	5.7	4.07	0.82	3.08	0.17	3.65	2.45	1.08	0.17
28	4776	4.0	2.72	0.59	2.08	0.20	2.63	1.76	0.67	0.20
26	4707	2.8	1.86	0.47	1.15	0.24	2.03	1.41	0.38	0.24
24	4639	2.0	1.17	0.38	0.53	0.26	1.59	1.15	0.18	0.26
22	4578	1.4	0.82	0.30	0.27	0.25	1.25	0.81	0.09	0.25
20	4517	1.1	0.59	0.26	0.10	0.23	1.08	0.77	0.03	0.23
18	4459	0.86	0.45	0.21	0.04	0.20	0.83	0.62	0.01	0.20
16	4404	0.70	0.36	0.17	0.01	0.18	0.69	0.51	—	0.18
14	4349	0.56	0.234	0.131	—	0.154	0.546	0.392	—	0.154
12	4296	0.45	0.237	0.111	—	0.126	0.460	0.334	—	0.126
10	4245	0.35	0.182	0.084	—	0.098	0.351	0.253	—	0.098
8	—	—	—	—	—	—	—	—	—	—

we usually make 100) we can then compare all the ordinates of the former with those of the latter, both being on the same scale. If the trichromatic theory holds good then the *difference* between the ordinates of the two curves should, at every place (except maybe in blue), in the case of incomplete red-blindness, give a curve which is mathematically similar to the normal red sensation curve. The ordinates of this curve compared with the ordinates of the normal red sensation curve will give the amount of red sensation *deficient* in the incomplete red-blind eye.

When the incomplete blindness is in the green sensation the same line of argument applies.

I give two cases, one of incomplete red- and the other of incomplete green-blindness. The measures were taken several years ago, and before I had worked out the three sensation curves of my own (normal) eye. Without knowing whether a comparison of the luminosity of the spectral colours to my own eye with the same white which they used for comparison purposes would be of any value, in some cases I made observations at the same time and recorded the readings. These I shall refer to later.

I must here point out that owing to differences in the absorption by the macula lutea in different eyes the blue sensation curve may not always be capable of the same treatment as the green or red sensation curves. But from the red end of the spectrum to about S.S.N. 40 (λ 5270)* this variation will not appreciably affect the results.

In Table III we have the case of the incompletely red-blind eye. The ordinates of luminosity as measured are given in Column III. We have to obtain a factor by which to multiply the numbers in this column to make it compare with the luminosity of normal vision given in Table I.

Table III.—Showing W.'s Curves.

I.	II.	III.	IV.	V.	VI.	VII.
Standard Scale No. (S.S.N.).	λ .	Luminosity.	Luminosity $\times 0.455$.	G.S. + B.S. from table.	Col. IV - V.	R.S. $\frac{1}{6}$.
60	6728	2.5	1.14	—	1.14	1.2
58	6521	7.9	3.59	0.21	3.88	3.5
56	6380	20.0	9.10	2.25	7.85	7.8
54	6152	42.5	19.32	7.60	11.72	12.0
52	5996	63	28.66	15.36	13.3	13.8
50	5860	82.5	37.5	25.00	12.5	12.5
48	5720	92.5	42.08	31.8	10.3	10.8
46	5596	92.5	42.08	32.8	9.3	9.1
44	5481	85.0	38.7	31.4	7.3	7.2
42	5378	73.0	33.2	27.8	5.4	5.8
40	5270	62.0	28.2	24.2	4.0	4.8
38	5172	47.0	21.4	16.5	2.9	2.9
36	5085	32.0	14.6	12.7	1.9	1.8
34	5002	20.0	9.1	7.97	1.1	1.0
32	4924	12.0	5.46	4.9	0.6	0.6
30	4848	8.0	3.64	3.3	0.34	0.41

Let us take S.S.N.'s 58 and 46 in the first instance. The normal luminosities of these S.S.N.'s are 21 and 87 (see Table I), and for W. 7.9 and 92.5.

* See "Colour Photometry," Part 3, 'Phil. Trans.,' 1890.

From these we can form two equations, putting z for the reduction of W.'s total luminosity curve and y for the reduction of his red sensation curve, the right-hand members of the equations being formed from the red sensations of these two scale numbers given in Table I. The left-hand member of the equations is the *difference* between the ordinates of the normal and red-blind curves at these scale numbers, which should be equal to the right-hand member.

$$\begin{aligned} 21 - 7.9z &= 21y, \\ 87 - 92.5z &= 54.2y. \end{aligned}$$

From these we find $y = 0.829$ and $z = 0.455$. Making x the factor by which the normal red sensation has to be multiplied in order to give the amount of this sensation that is present in W.'s colour sense $x = 1 - y$, and from these equations $x = 0.171$. That is when his curve is multiplied by 0.455, the difference between the ordinates of his curve and those of the normal give a curve which is five-sixths of the normal R.S. curve.

Taking two other positions, viz., S.S.N.'s 50 and 44, we obtain the following equations:—

$$\begin{aligned} \text{S.S.N. 50} \dots\dots\dots 100 - 82.5z &= 75y, \\ \text{S.S.N. 44} \dots\dots\dots 75 - 85z &= 43.6y + 0.1^* \end{aligned}$$

From this we obtain $z = 0.455$, $y = 0.84$, $x = 0.16$. Taking the mean of y , we get

$$y = \frac{1}{2}(0.84 + 0.83) = 0.835 \quad \text{and} \quad x = 0.165;$$

that is, W. has only 0.165 or closely $\frac{1}{6}$ R.S.

This number has been used in the table to compare the red sensation curve of the table with that of the incomplete blind.

Column I is the S.S.N., II the wave-length λ , III the luminosity of the colour-blind, IV the Column III $\times 0.455$, V (G.S. + B.S.) from the Table I; VI is (Column IV — Column V), and Column VII $\frac{1}{6}$ R.S. reduced from Table I. It will be seen that after the (G.S. + B.S.) have been deducted from the reduced luminosity, we have a residue which gives (within limits of error of observation) the same numbers as those given by $\frac{1}{6}$ R.S. In this case, then, the incomplete blind luminosity curve indicates the truth of the trichromatic theory, and also of the sensation curves of Table I obtained by the author. The nearer to complete colour-blindness, the greater the necessity for accuracy in the determination of the luminosity curves. In the next table is given a determination of a case of incomplete green-blindness, N.

Table IV.—N.'s Curves.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Standard Scale No., S.S.N.	λ .	Original luminosity readings by N.	Luminosity readings from diagram.	Luminosity $\times 0.82$.	Luminosity of R.S. + B.S. from Table.	Col. V—VI showing N.'s G.S.	G.S. 0.086 from Table.
60	6728	8.7	8.7	7.18	7	0.13	—
58	6521	25.5	25.5	20.90	20.79	0.11	0.18
56	6330	58.5	58.5	47.97	47.75	0.22	0.19
54	6152	87.5	89.0	72.98	72.40	0.58	0.51
52	5996	100	100	82.00	80.64	1.36	1.32
50	5850	93.5	94	77.08	75.00	2.08	2.15
48	5720	82.8	82.5	67.65	65.23	2.42	2.78
46	5596	69.6	69.6	57.07	54.29	2.78	2.61
44	5481	57	56.5	46.83	43.69	2.64	2.69
42	5373	46	45	36.90	34.73	2.17	2.38
40	5270	32.2	34	27.88	25.91	1.97	2.07
38	5172	23.7	23.7	19.43	17.59	1.34	1.60
36	5085	15	15	12.30	11.19	1.11	1.10
34	5002	8.8	8.5	6.77	6.34	0.43	0.68
32	4924	4.8	4.7	3.94	3.72	0.22	0.41
30	4848	3.2	3.5	2.87	2.62	0.25	0.26
28	4776	2.6	2.6	2.13	1.96	0.17	0.17
26	4707	2.2	2.1	1.72	1.65	0.07	0.09
24	4639	1.8	1.8	1.43	1.41	0.02	0.04
22	4578	1.5	1.5	1.23	1.10	0.13	0.02
20	4517	1.3	1.3	1.06	1.00	0.06	0.08

Taking S.S.N.'s 52 and 46, we form the following equations as before; but from Table I we use the green sensation luminosity—

$$\text{S.S.N. 52} \dots\dots\dots 96 - 100z = 15.36y.$$

$$\text{S.S.N. 46} \dots\dots\dots 87 - 69.6z = 32.7y + 0.1.*$$

From these we find

$$z = 82, \quad y = 0.914 \quad \text{and} \quad x = 0.086.$$

Other pairs of equations can be formed by, say, S.S.N.'s 52 and 38:—

$$\text{S.S.N. 52} \dots\dots\dots 96 - 100z = 15.36y,$$

$$\text{S.S.N. 38} \dots\dots\dots 35.9 - 23.7z = 18.43y.$$

From which we get

$$z = 0.82, \quad y = 0.89 \quad \text{and} \quad x = 0.11.$$

We may take y as 0.90 approximately, which tells us the green sensation felt is only about one-tenth of the normal. [The green sensation is shown in the table as 0.086 of the normal.]

* B.S.

This method can be used in what at first sight appear to be complicated cases, but it was not possible to use it before the sensation curves of normal vision had been worked out, as unless the composition of the colours in terms of sensation luminosity is known, y must also remain unknown.

A case which puzzled those who considered it, is shown in the 'Roy. Soc. Proc.' May 14, 1891, vol. 49. The figure is not well drawn, but the numbers given in the table of luminosities are correct.*

The readings near the maximum were a little erratic, probably owing to the fact that at that part green was distinguished, the rest of the spectrum being grey or brownish-grey. Using numbers on each side of the maximum to form our equations, the following are found to give the factors of reduction of the curve to compare it with the normal curve whose maximum is 100. Taking S.S.N.'s 56 and 40, we form the first pair of equations from the luminosities in Table I and that of N. W.'s luminosities. As before, the right hand of the equations are formed from the R.S. numbers in Table I.

$$50-30z = 47.7y, \quad 50-62.5z = 25.8y.$$

This gives $y = 0.73, \quad z = 0.51.$

Another pair of equations can be formed from S.S.N.'s 54 and 44—

$$80-52z = 72.4y, \quad 75-88z = 31.3y,$$

which give $y = 0.69, \quad z = 0.56.$

From S.S.N.'s 52 and 42 we get

$$96-70z = 80.6y, \quad 62.5-72z = 34.6y,$$

which make $y = 0.74, \quad z = 0.52.$

From S.S.N.'s 58 and 46 we get

$$21-10z = 20.8y, \quad 87-90z = 54.2y,$$

which make $y = 0.77, \quad z = 0.5.$

From S.S.N.'s 60 and 38 we get

$$7-3z = 7y, \quad 36-46z = 17.5y,$$

which make $y = 0.78, \quad z = 0.57.$

The mean of the different values of y is 0.74,

And that of the different values of z is 0.53.

For the sake of simplicity, we may take the values as $y = 0.75$, that is, x (the red sensation) is 0.25 of the normal, $z = 0.50$. In Table III these values are employed. It also, in Column V, gives the theoretical curve derived from Table I containing the colour equations.

* At S.S.N. 42, 82 was a misprint for 72.

Table V.—Showing N. W.'s Curves.

I.	II.	III.	IV.	V.
Standard Scale Nos., S.S.N.	λ .	N. W.'s luminosity.	N. W.'s luminosity $\times 0.5$.	Luminosity from Table I, R.S. being 0.25 of normal.
62.5	7020	0	0	0
60	6728	3	1.5	1.75
58	6521	10	5	5.4
56	6380	30	15	14.2
54	6152	52	26	25.7
52	5996	70	35	35.6
50	5850	81	40.5	43.7
48	5720	87	43.5	48.1
46	5596	90	45	46.3
44	5481	88	44	41.8
42	5373	72	36	36.5
40	5270	62.5	31.2	30.5
38	5172	46	23	22.9
36	5085	23	11.5	12.4
32	5002	12.5	6.25	5.67
31	4985	10	5	4.67
25	4676	5	2.5	1.41
20	4517	3	1.5	0.52
15	4377	2.5	1.25	0.28
10	4245	1.5	0.75	0.16
0	4010	0.2	0.1	0.014

Comparing Columns IV and V together, we see that at the position of maximum luminosity the theoretical values differ from those obtained from the readings, the mean of which was taken. Had the evidently low readings been omitted when calculating the mean, the two would have tallied well. A further examination of these two columns also shows that at the violet end of the spectrum the luminosity values obtained by N. W. are much larger than the normal curve gives.

The luminosity of the blue sensation is very small compared with the luminosities of the red and green, and is negligible as far (say) as S.S.N. 30, but from S.S.N. 25 to the violet end the luminosity of the blue sensation plays a larger and larger part in the total luminosity of each scale number.

We have already found the factor of the red sensation (which forms part of the normal violet). If then from the luminosity values obtained by N. W., we subtract her reduced red sensation, and also the whole of her green sensation, the residue will be due to the blue sensation, which can be compared with that existing in normal vision.

Taking her readings from S.S.N. 25 to 0, we obtain the following result:—

S.S.N.	N. W.'s luminosity.	N. W.'s reduced red sensation.	G.S.	N. W.'s B.S.	Normal B.S.	N. W.'s B.S. Normal B.S.
0	0·10	0·014	—	0·086	0·022	4·0
10	0·75	0·06	—	0·64	0·1	6·4
15	1·25	0·11	—	1·14	0·16	7·0
20	1·5	0·2	0·1	1·25	0·234	5·8
25	2·5	0·32	0·84	1·84	0·25	5·4

If we lay down the luminosities shown in a curve, and draw a freehand curve between the points, we get $0 = 0·15$, $10 = 0·7$, $15 = 1·1$, $20 = 1·65$, $25 = 2·6$ as ordinates, and the resulting ordinates of N. W.'s blue sensations are six times larger than those of the normal curve.

It appears likely that the blue sensation is the same as the normal, and that the green sensation is reduced to one-sixth of the normal and the red to one-twenty-fourth. These facts give a very good clue to the naming of the colours of the spectrum as given in the paper referred to.

One more example of the application of the formula to complete red-blindness may be given. At p. 466, 'Roy. Soc. Proc.' 1910, where the first part of this subject is treated of, we have the luminosity curve of X taken direct in Column IX of the table. We can apply the formula as in the other cases. Taking S.S.N.'s 50 and 40,

$$50 \text{ gives } 100 - 25z = 75y,$$

$$40 \quad \text{,,} \quad 50 - 24z = 25·8y.$$

Here $y = 1$ and $z = 1$. That is, as $x = 0$, the colour-blindness to red is complete.

Taking S.S.N.'s 52 and 38, we get

$$52 \text{ } 96 - 15·1z = 80·6y,$$

$$\text{and } 38 \text{ } 36 - 18·5z = 17·5y.$$

Here again $y = 1$ and $z = 1$, and from this pair the same deduction is made.

We can now discuss the plan of calculating *directly* the amount of colour sensation which exists in an incompletely colour-blind eye. The method is adapted also for the completely colour-blind. Suppose a person with normal vision and the person whose colour-vision is defective each make luminosity measures of the same spectrum colours, the comparison white light in each case being the same. (The luminosity, it must be remembered, is measured by sectors placed in the path of the white beam.) Now the luminosity of the white light to the colour-blind is less than to normal eyed by exactly the amount due to the defect in one sensation. Hence, when the colour-blind

makes an observation, he is making the comparison with a lower luminosity of white than does the observer with normal vision. If the white light were to both equally luminous their readings would give two curves of such a character that the difference in ordinates would be a direct measure of the defect as in the previous method. As the white light is less luminous to the colour-blind, we have to find to what extent the ordinates of his curve have to be altered.

Let x be the factor giving the amount of his deficiency in one sensation, and let m , n and r be the component luminosities of the red, green, and blue sensations of the ray which is to be measured.

Reverting to Table I the total luminosities of these three sensations in the whole spectrum of white light to normal vision are closely as 580, 250, and 3. It will be seen that the blue luminosity has but small effect, and the red and the green are nearly as 7 to 3, when the luminosity for the normal eye is 10. In those rays of the spectrum which contain the defective sensation the luminosity of this sensation must be multiplied by a factor x . Supposing the reading for the normal to be a , and for the colour-blind b , then we can make an equation which will contain x . To the red-blind n remains unaltered, and r is negligible, so that we get the equation in the form

$$\frac{a(mx+n)}{m+n} = \frac{b(7x+3)}{10}, \quad (i)$$

from which x can be determined. When there is no green sensation in the colour, as when the slit is at any scale number below 58, the equation becomes

$$ax = \frac{b(7x+3)}{10}. \quad (ii)$$

For a green-blind m remains unaffected, and the equation (i) becomes

$$\frac{a(m+nx)}{m+n} = \frac{b(7+3x)}{10}, \quad (iii)$$

and equation (ii) becomes $a = \frac{b(7+3x)}{10}$. (iv)

Supposing $x = 0$, which is the case when the colour-blindness to red or green is complete, (i) becomes

$$\frac{an}{m+n} = \frac{3b}{10} \quad \text{or} \quad b = \frac{10an}{3(m+n)},$$

and (iii) becomes $\frac{am}{m+n} = \frac{7b}{10}$ or $b = \frac{10am}{7(m+n)}$.

[$(m+n)$ is, of course, the luminosity from the normal curve Table I.]

(iv) becomes $a = \frac{7b}{10}$ or $b = \frac{10a}{7}$,

which shows that the readings in the red are larger for the green-blind than for normal vision.

The following observations made by a well-known man of science are given in Table VI and show the application of both methods of procedure.

Table VI.—Showing Z's Curves.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Standard Scale No., S.S.N.	λ .	Luminosity of Z from diagram.	Luminosity of Z $\times 0.7$.	Luminosity calculated from Table. R.S. being 0.35.	A's observation.	Standard Scale No., S.S.N.	Original observation.
60	6728	3.5	2.45	2.45	8	59.6	5
58	6521	12	8.4	8.38	25	57.6	16
56	6330	27	18.9	19	50	55.6	34
54	6152	47	32.9	32.9	68	53.6	53
52	5996	62	43.4	43.6	79	51.6	65
50	5850	73	51.1	51.2			
48	5720	77	53.9	53.9	—	49.6	74
46	5596	74	50.8	51.7	—	47.6	76
44	5481	67	46.9	46.8	—	45.6	71
42	5373	57	39.9	39.8	—	43.6	64
40	5270	47	32.9	33.2	—	41.6	54
38	5172	35	24.5	24.55	—	39.6	44
36	5085	24	16.8	16.72	—	37.6	30
34	5002	15	10.5	10.16	—	35.6	19
32	4924	8	5.6	6.17	—	33.6	11
30	4848	4.5	3.15	4.06	—	31.6	7
					—	29.6	4

We will ascertain the *defect* of red sensation by the first method, and then confirm it by the second method. From the following table we take the scale numbers 52 and 46 :—

$$96 - 62z = 80.6y, \quad 87 - 74z = 54.2y.$$

From this $y = 0.67, \quad z = 0.68.$

$$\text{S.S.N.'s 50 and 66 give } 100 - 73z = 75y, \quad 50 - 27z = 47.7y.$$

This makes $y = 0.65, \quad z = 0.7.$

From S.S.N.'s 54 and 40

$$80 - 47z = 72.4y, \quad 50 - 47z = 25.8y.$$

From this $y = 0.64, \quad z = 0.72.$

Taking the mean of these factors, we get

$$y = 0.65, \quad z = 0.7.$$

Here we have the *defect* in the red sensation is 0.65; therefore, he must have only 0.35 R.S. of normal vision.

Using formula (i), at S.S.N. 59.6 the luminosity of the normal vision is 8, and of the colour defective 5.

$$8x = \frac{5(7x+3)}{10}, \quad x = 0.33.$$

At another place in the red the readings were 25 and 16.

$$25x = \frac{16(7x+3)}{10}, \quad x = 0.35.$$

At 55.6 the normal and colour-blind readings were 50 and 34. In this case $m = 52.7$ and $n = 3.3$. The equation then becomes

$$\frac{50(52.7x+3.3)}{56} = \frac{34(7x+3)}{10}.$$

This makes $x = 0.31$.

Again, at 53.6 the two readings were 68 and 53. The equation is then

$$\frac{68(74x+9.2)}{83.2} = \frac{53(7x+3)}{10}.$$

This gives $x = 0.376$.

Finally, at 51.6 the readings are 79 and 65. The equation is

$$\frac{79(79.5x+17.4)}{96.9} = \frac{65(7x+3)}{10}.$$

This makes $x = 0.33$.

The mean of the separate results gives 0.34 as the factor by which to reduce the sensation of this incompletely red-blind. The factor derived from the first method was 0.35. This example shows that both methods give the same result.

I have worked out the sensation factors from numerous other luminosity curves as made from the observations of incompletely colour-blind persons. So far, I have not met with any case to which these methods, founded on the normal colour sensations, as shown in Table I, will not apply. Any small deviations which are shown, are readily accounted for by errors in the somewhat difficult measure of luminosity. Whatever may be the nature of the visual receiving apparatus, whether it be mechanical or chemical, there seems to be no reason why similarity in the sensation curves of the colour-blind, compared with those of the normal curves, should not always be maintained. It is probable that, taking the wave-lengths and energy of the different points in the spectrum curves, the normal visual sensation curves can be calculated.

I now give a determination of the amount of incomplete colour-blindness which existed in a recent case that came before me for examination. In addition to ordinary tests I employ, and of which I shall have to say something in another communication, the luminosities of two points in the spectrum were determined by the colour-blind (Jn.) and myself. It was found by the examination that he was red-blind to a certain extent, and afterwards the amount was determined by the two sets of observations.

At S.S.N. 34 Jn.'s luminosity was 21, that of A 45.5,*

" 56.7 " " 28 " 43

At S.S.N. 34 the sensation luminosities from the table were

R.S. G.S.
6.22 + 7.98,

and at S.S.N. 56.7 R.S. G.S.
38.45 + 1.55.

The following equations were formed to determine the *defect* in red sensations :—

$$14.2 - 21z = 6.22y, \quad 40 - 28z = 38.45y.$$

From which y , the factor of defect, was 0.7, or 0.3 was the amount of his red sensation, and z , the factor by which to reduce the luminosity, was 0.47.

Next using my determinations of the luminosity, the following equations were obtained, where x is the factor for R.S. existing in Jn.'s sensation :—

$$\frac{43(38.45x + 1.55)}{40} = \frac{28(7x + 3)}{10}, \quad x = 0.314.$$

$$\frac{15.5(6.22x + 7.98)}{14.2} = \frac{21(7x + 3)}{10}, \quad x = 0.29.$$

The mean of the two gives 0.3 as the factor and agrees with the preceding determination. It is to be noticed that the blindness must be to the red, for if we form equations by the first method, supposing green-blindness, with the same numbers we get

$$14.2 - 21z = 7.98y, \quad 40 - 28z = 1.55y.$$

This makes y a minus quantity, which is impossible.

Again, with the second method we should have, with S.S.N. 57.6

$$\frac{43(38.45 + 1.55x)}{40} = \frac{28(7 + 3x)}{10}.$$

We get x larger than unity.

There is at least one other method by which the amount of visual defect in a colour sensation can be determined, but this is dependent on the colours

* In both cases the mean of several observations was taken.

which go to form white. This and the colours perceived by the colour-blind and by normal vision I have reserved for a future communication.

There may be some investigators who are using a low grade of artificial light such as paraffin, candle, or the glow lamp. They do not differ much from one another, so I have thought it might be of use if I gave the luminosity curve of the spectrum of the light emitted by paraffin (crystal oil). I have also shown the luminosities in terms of R.S., G.S., and B.S. in Table VII. It will be noticed that the maximum of R.S. is at S.S.N. 54 instead of at S.S.N. 52, as is the case if the arc light is used, and the maximum G.S. is at S.S.N. 48 instead of at S.S.N. 46, as also is the case for the arc light.

Table VII.—Luminosity Curves of the Spectrum of a Paraffin (Crystal Oil) Light.

I.	II.	III.	IV.	V.	VI.
S.S.N.	λ .	Luminosity.	R.S.	G.S.	B.S.
64	7217	1	1	—	—
62	6957	3·4	3·4	—	—
60	6728	11·27	11·27	—	—
58	6521	81·3	31	0·82	—
56	6380	65	62·07	2·93	—
54	6152	95·7	88·61	7·09	—
52	5996	100	84·2	15·8	—
50	5850	89·2	66·9	22·3	—
48	5720	69·4	46·57	22·82	0·018
46	5596	52·7	32·82	19·61	0·055
44	5481	39	22·66	15·27	0·062
42	5378	28·1	15·56	12·45	0·065
40	5270	20	10·31	9·64	0·044
38	5172	13·2	6·42	6·74	0·033
36	5065	8	3·68	4·19	0·033
34	5002	4·2	1·76	2·32	0·036
32	4924	2·2	0·98	1·2	0·037
30	4848	1·32	0·55	0·67	0·042
28	4776	0·84	0·37	0·42	0·045
26	4707	0·52	0·26	0·21	0·046
24	4689	0·35	0·20	0·1	0·047
22	4578	0·22	0·144	0·036	0·039
20	4517	0·15	0·106	0·012	0·032

This indicates the extreme care that must be taken in securing a good luminosity curve of the spectrum of the light employed for investigations before any deductions as to observations are made.

In a paper recently presented to the Royal Society on the subject of

colour-blindness there are several misapprehensions of what the trichromatic theory can or cannot explain. One very glaring misapprehension is that this theory cannot explain the matching of a bluish green by a mixture of red and blue. This is one of the most easy matches to make by the green-blind, for the green of the normal spectrum curves is absent to the green-blind, and the overlapping curves at this point are red and blue (see S.S.N. 34, Table I, which is a blue-green). Hence a mixture of red and blue to the green-blind will match what is blue-green to normal vision. There are other points on which there are misapprehensions, and they will be dealt with in another communication which I propose to offer.

On the Sensibility of the Eye to Variations of Wave-length in the Yellow Region of the Spectrum.

By Lord RAYLEIGH, O.M., F.R.S.

(Received November 26,—Read December 8, 1910.)

Dr. Edridge-Green* has introduced a method of classifying colour-vision by determining the number of separate parts or divisions in the spectrum within each of which the observer can perceive no colour difference. Movable screens are provided in the focal plane of the spectroscopic telescope, by which the part admitted to the eye is limited and the limits measured in terms of wave-length. Beginning at the extreme visible red, more and more of the spectrum is admitted until a change of colour (not merely of brightness) is just perceptible. This gives the first division. The second division starts from the place just determined, and is limited in the direction of shorter wave-length by the same condition. In this way the whole spectrum is divided into a number of contiguous divisions, or patches, which Dr. Edridge-Green terms monochromatic. It will be observed that the delimitation of these patches includes an arbitrary element depending on the point from which the start is made—in this case the extreme red.

“Tested with this instrument a normal individual will, as a rule, name six distinct colours (viz., red, orange, yellow, green, blue, violet), and will mark out by means of the shutters about 18 monochromatic patches. Occasionally we come across individuals with a greater power of differentiating hues, to whom, as to Newton, there is a distinct colour between the

* ‘Roy. Soc. Proc.’ B, 1910, vol. 82, p. 458, and earlier writings.

blue and violet, which Newton called indigo. Such individuals will mark out a greater number of monochromatic patches, from 22 up to 29. The limited number of monochromatic patches which can be marked out in this way is at first surprising when we consider how insensibly one part of the spectrum seems to shade into the next when the whole of the spectrum is looked at. The number and position of the patches present, however, great uniformity from one case to another."

Being curious to know into what class my own vision would fall on this system, I was glad to be tested by Dr. Edridge-Green last July. The number of patches proved to be 17, a little short of the number he lays down in the passage above quoted as normal. The slight deficiency appears to be in the high violet. I have known for some years that I required more light in the violet to measure interference-rings than did my assistant, Mr. Enock, and that the deficiency of sensibility was greatest for my right eye, used with Dr. Green's apparatus. The limits of the actual patches were as follows:—

780—635½—624—612—603—595—586—576—560—541—521—509—
500—489½—477—462—443—426.

Thus in the region of the D lines a patch including wave-lengths between 595 and 586 did not manifest a difference of colour. The interval between the D lines on the above scale being 0.60, it appears that my "monochromatic patch" was 15 times this interval.

While it is undoubtedly true that in this way of working no colour-difference was perceptible as the eye travelled backwards and forwards over the patch, my experience with colour discs and other colour-mixing arrangements made me feel certain that under more favourable conditions I could discriminate much smaller differences of wave-length. Special experiments have since proved that I can in fact discriminate by colour between points in the spectrum as close together as the two D lines.

In order to compare two colours with advantage it is necessary that each should extend with uniformity over a considerable angular area, and that the two areas should be in close juxtaposition. The requirements of the case are sufficiently met by a colour-box (after Maxwell) such as I described nearly 30 years ago.* In this form of apparatus a second slit, placed at the focus, allows a narrow width of the spectrum to pass; but instead of regarding the transmitted portion with an eyepiece, the eye is brought close to the slit and focussed upon the prism, which thus appears uniformly lighted with such rays as the second slit allows to pass. The light thus

* 'Nature,' 1881, vol. 25, pp. 64—66; 'Scientific Papers,' vol. 1, p. 543. See also 'Nature,' August 18, 1910.

presented is of course not absolutely homogeneous; it includes a mixture of neighbouring spectrum rays, the degree of purity augmenting as the slits are narrowed. With the aid of a refracting prism of small angle (set perpendicularly to the dispersing prisms) the field of view is divided into two parts which correspond to any desired colours according to the situation of the two primary slits. For the present purpose these primary slits lie nearly in one straight line, inasmuch as the two spectrum colours to be compared are close together.

A detail of some importance in delicate work may here be mentioned. It is known that in many cases, *e.g.* in lantern projection, the spectrum lines corresponding to a straight primary slit are sensibly curved. Mr. Madan proposed many years ago to cure this defect by counter-curving the primary slit. In the kind of instrument under discussion it is desirable to retain straight primary slits, but there is nothing to forbid curvature of the second or eye slit, which is a fixture, and such curvature is necessary for the most effective working. A deficiency in this respect, or in focussing, may entail objectionable changes of colour as the eye moves about behind its slit. The simplest way of making the adjustment is to illuminate a somewhat narrow primary slit with soda light and to fit the jaws of the secondary slit to the image thus obtained and examined with a lens as eyepiece.

In making the observations on sensitiveness, one primary slit, as well as the eye-slit, remains fixed, the position being chosen so as to provide yellow light from the neighbourhood of D. The second slit can be moved as a whole while retaining its width. The shutters necessary were cut from thin zinc sheet and were held by sealing or soft wax, in a manner which need not be minutely described. The movements of the shutter which carries the second slit were measured by callipers.

The procedure is quite simple. If the colours seen are strongly contrasted, the movable slit is displaced until the difference is moderate. Marks may then be given; 0, denoting that the difference is uncertain; R_1 , that it is just distinct in the direction of making the second patch the redder; G_1 , that it is just distinct in the opposite direction. Similarly, R_2 , G_2 , denote differences in the two directions which are more than distinct, and so on. After each observation worth recording, the position of the movable slit is measured.

One further precaution ought to be mentioned. In making a decision when the difference of colour is slight, care should be taken that the brightnesses are nearly equal. When, as in my experiments, daylight is employed, the passage of clouds may cause a disturbance in this respect, even if the two primary slits are of equal width. The interposition of a

piece of ground glass a little behind the primary slits is usually a remedy. But this reduces the illumination, and it is sometimes preferable to adjust the brightness otherwise. It may be done conveniently by cutting off some of the light on the preponderating side by the interposition of one or more strips of glass held at varying angles of obliquity.

In this manner, as the result of sets of observations made on several days, it was found that a movement of the second slit through 0.15 mm. was sufficient to carry the variable colour from being distinctly redder than the standard to distinctly greener. No doubt the result might have been arrived at quicker with a more refined apparatus, in which the movements of the slit were controlled and measured by a micrometer screw, but I do not think it would be any more certain. Probably the distance is something of an over-estimate. In several of the measurements included, the distinctness of the difference was unnecessarily pronounced. We may conclude that the eye is capable of appreciating without fail a difference of situation represented by 0.07 mm.

It remains to interpret the result in terms of wave-lengths. By allowing light to enter at the eye-slit, or rather at a narrower slit superposed upon it, a spectrum is formed at the other end whose scale has to be determined. It appeared that the distance from D to E was 7 mm. The difference of wave-length between these lines is 62.3. The perceptible difference is 1/100 of this, corresponding nearly enough to the difference between the D lines. I think I am safe in saying that I could distinguish the colours of the two D lines if favourably presented to the eye.

This degree of sensitiveness, though not higher than I had expected, is a little difficult to reconcile with the monochromatic appearance of a portion of the spectrum 15 times wider. I suppose that the gradual character of the transition is an obstacle to the recognition of differences. The question of angular magnitude may also enter. No doubt a very small apparent magnitude would be unfavourable. It is possible that in Dr. Green's apparatus an eyepiece of higher power, with a corresponding augmentation in the intrinsic brilliancy of the source of light, would allow of an increase in the number of distinguishable patches. The experiment would be worth a trial.

It will be seen that the existence of "monochromatic patches" in the spectrum is far from meaning that the eye is incapable of making chromatic distinctions within their range. I do not infer from this that the results of the method are without significance. Undoubtedly it is possible by means of it to classify colour-vision, and such a classification cannot be without interest, even if we fail as yet to understand exactly what it means.

In conclusion, I will remark that those who lay great stress upon the number of principal colours recognised by any particular eye seem to me to overlook too much the colours not represented in the spectrum. To most of us *white* is a sensation quite as distinct from any other as yellow can be. In my estimation purple has a better claim than orange to be reckoned a principal colour. The fact, too, that dark orange reveals its character so little as to be called by another name (brown) seems to indicate that these distinctions are not of fundamental importance.

On the Determination of the Chief Correlations between Collaterals in the Case of a Simple Mendelian Population Mating at Random.

By E. C. SNOW, B.A., Biometric Laboratory, University College, London.

[This paper is published in 'Proceedings,' Series B, vol. 83, pp. 37—55.]

*Address of the President, Sir Archibald Geikie, K.C.B., at
the Anniversary Meeting on November 30, 1910.*

The year which has passed since our last Anniversary will be memorable in our annals for the losses which death has brought upon the Royal Society. First and most conspicuous is the decease of our Patron, His revered Majesty, King Edward VII. During his brief but eminently beneficent reign, His Majesty continued to manifest the same interest in the advancement of science which he had always shown before his accession to the Throne. We mourn that a life so devoted to the cause of peace and progress should have been cut off so soon. King George V has honoured us by stepping at once into his father's place as Patron of the Royal Society, and has subscribed his name in our Charter-book. His Majesty as Prince of Wales found many occasions to show his appreciation of science, and his interest in its progress. We feel confident that under his enlightened rule the advancement of Natural Knowledge will continue to receive his support and encouragement.

The deceased Fellows are :

Dr. Ludwig Mond, died December 11, 1909.
Dr. Shelford Bidwell, died December 18, 1909.
Sir Charles Todd, died January 28, 1910.
Edward Saunders, died February 6, 1910.
Sir Robert Giffen, died April 12, 1910.
Sir William Huggins, died May 12, 1910.
John B. N. Hennessey, died May 23, 1910.
C. Greville Williams, died June 15, 1910.
The Rev. Robert Harley, died July 26, 1910.
Dr. Sydney Ringer, died October 14, 1910.

The deceased Foreign Members are :

Prof. Friedrich Kohlrausch, died January 17, 1910.
Prof. Eduard F. W. Pflüger, died March 17, 1910.
Prof. Alexander Agassiz, died March 28, 1910.
Prof. Stanislao Cannizzaro, died May 10, 1910.
Prof. Robert Koch, died May 27, 1910.
Prof. Giovanni Schiaparelli, died July 4, 1910.
Dr. Melchior Treub, died October 3, 1910.

On the list of Foreign Members of the Society we have thus to mourn the loss of no fewer than seven illustrious names. Of these there is none which we

more deeply regret than that of ALEXANDER AGASSIZ. His frequent visits to Europe brought him into closer personal contact with the Fellows of the Royal Society than is usually possible for our Foreign Members. Only last summer he came once more among us with apparently little diminution of his characteristic capacity for work. But it was his last public appearance, for he died a week or two afterwards on his homeward passage across the Atlantic.

His genius for original research, the unwearied activity with which he pursued those lines of enquiry to which he specially devoted himself, and the generous prodigality with which he placed his ample fortune at the service of science in the investigations which he led and inspired, placed him at the head of the oceanographers of his day. Year after year he traversed, dredged, and sounded the ocean through many different latitudes, bringing back from each cruise enormous collections of material, which went to increase the treasures of that Museum of Comparative Zoology which his father had planned at Harvard, and to which he himself had devoted the strenuous energies of his life. Besides adding much to our knowledge of the fauna of the deep, he ever had an eye for the great physiographic problems which the oceans, their coasts, and their islands present. The pile of goodly volumes in which his incessant labours are chronicled form one of the most remarkable monuments which have been reared in our day by the genius, enterprise, and enthusiasm of a single man.

By the death of STANISLAO CANNIZZARO, at the ripe age of 84, Italy has been deprived of her foremost chemist, and science has to regret the loss of one of her illustrious students, who by his generalisations on chemical combination did so much to place modern chemistry on a sound basis. It happened that at the time of his death the senior Secretary of the Royal Society and myself were in Rome as delegates of the Society to the meeting of the International Association of Academies. We were glad to avail ourselves of the opportunity of attending the funeral of our deceased Foreign Member. It was a touching sight to find that in the class-room where he had so long taught and where his diagrams were still hanging on the walls, the coffin had been placed on his lecture-table and was guarded by a body of his students, who bore it thence on their shoulders, through a dense crowd of mourners to the hearse. Representatives of science from far and near followed the body to the grave.

A veteran astronomer has passed away in GIOVANNI SCHIAPARELLI. From the time of his discovery of the planet Hesperia, made when he was only six and twenty years of age, he prosecuted an active and successful study of the heavens, extending over some forty years at the observatory of Milan.

His notable identification of the orbits of meteors with those of comets, his minute delineation of the surface of the planet Mars, and his subsequent studies of Mercury and Venus, have made his name a household word in astronomical science.

In ROBERT KOCH we have to deplore the loss of one who conferred inestimable benefits on the science of bacteriology. To him we owe the isolation of the tubercle bacillus, the proof that it is the cause of tuberculosis, and the product, tuberculin, for the treatment of this calamitous disease. He has made modern bacteriology possible by his elaboration of methods for the culture of bacilli.

FRIEDRICH WILHELM KOHLRAUSCH, who died in January last, in his seventieth year, will be remembered for his investigation of the methods of measuring magnetic and electrical quantities, for his laborious researches into the conducting power of electrolytic solutions, which formed the foundation of the modern electrolytic theory of solution, and for the great service which he rendered by insisting on the necessity of practical instruction in the laboratory for the teaching of physics.

In MELCHIOR TREUB botany has lost an esteemed and eminent worker. A master of technique, with high intellectual gifts, he attacked many important problems and materially advanced knowledge in the diverse domains of plant physiology, cytology, morphology and geography, presenting his results with great lucidity and grace of style. His scientific work was mainly done while he was engrossed in the official duties of Director of the Buitenzorg Botanic Garden in Java: duties performed for nearly thirty years with such success that the practical benefits which resulted from them to pharmacology, forestry and tropical agriculture are comparable with his scientific contributions. His sympathies were as wide as his interests; and his memory will live in the work which he helped others to achieve as well as in his own.

Coming now to the losses from our Home List during the year that has passed, we have to mourn the death of one of the great historical figures of the Royal Society—SIR WILLIAM HUGGINS. It would be out of place in this brief address to attempt even a summary of the achievements of his distinguished career, but on this anniversary occasion our thoughts naturally turn to the recollection of the salient features of that career which shed such lustre on the Society. Soon after the invention of spectrum analysis as a practical method of investigation was accomplished, only fifty years ago, by Kirchhoff and Bunsen, Huggins resolved to devote himself to the application of this new method to astronomical problems, and, as we all know, he thereby laid the foundations of the wonderful science of astrophysics. His early observations of the spectra of the stars, made before any of the apparatus

now so appropriate for such purposes had been evolved or even thought of, showed his close application and the exquisite refinement of his appliances. In rapid succession he informed us of the similarities in constitution between some types among the fixed stars and our own Sun, and of the marked differences shown by other types, thus leading on to the great fundamental subject of the classification of the stars and initiating the discussion of the order of their evolution. The early application of photography to the spectra of objects whose light is so feeble demanded wonderful patience and skill: it was rewarded with an immediate crowd of physical results in the registration of spectra far beyond the visible limit in the violet, among which the recognition of the second spectrum of hydrogen may be recalled. So, too, at a later time, when the four lines of the ordinary spectrum of this gas were shown by Balmer to belong to a very definite algebraic series, which ought to include numbers of other lines whereof laboratory experiments showed no trace, it was Huggins who called in the aid of the celestial laboratory of the stars and pointed to the exact succession of the missing lines in the spectra of certain stars—thereby infusing new zeal into the efforts of theorists to unravel the secret of the origin of the spectrum.

When the same refined appliances were turned to the scrutiny of the nebulae, which are spread over such vast regions of the sky, the news soon came that the problem raised by William Herschel and his successors had now been definitely solved by the discovery that these nebulae were not all clusters of stars, but that some of them shone as masses of glowing gas. In solar work reference may be made to Huggins' proposal to render the flame-prominences visible in open day by great optical dispersion, and also, though the result was less satisfactory, to his persistent attempts to photograph the solar corona by aid of coloured screens. But perhaps the most brilliant of his achievements was his early conception, undeterred by full knowledge of the difficulties which had to be faced, that it might be possible to measure the velocities of approach or recession of the stars by spectroscopic means. In a masterly investigation he proved to the world that his expectation was well grounded, and that the development of instruments specially adapted for this new outlook into astronomy demanded vigorous prosecution. His other laboratory work, all designed for the elucidation of astronomical problems, can only be referred to, such, for instance, as his research into the nature of the luminosity of radium salts.

Sir William Huggins was elected into the Royal Society as far back as 1865. During his long association with us he took the keenest interest in the affairs and the success of the Society. He was repeatedly elected into the Council, where his total length of service amounted to no less than sixteen

years. He served as Vice-President for four years, and we count it as one of the distinctions of the Society in our time that he held the office of our President for five years. Thus, not merely for the lustre reflected from his high reputation in science, but for the personal service which he so willingly and effectively rendered in the conduct of its business, the Royal Society gratefully and affectionately cherishes his memory.

But, great as was his position in scientific discovery, it is within the personal knowledge of most of us that in character he was equally great. His was an ideal life, dedicated throughout to the sublime science for which he did so much, and during many years happy in the devoted companionship and co-operation that eased, and at the same time stimulated, the arduous work of a solitary astronomer.

DR. LUDWIG MOND will be remembered not only for his eminence in chemistry, which was recognised by his election into this Society, but for the indomitable courage and sagacity with which he brought his discoveries into successful practical operation on a commercial scale, and not less for the well-considered and large-hearted liberality wherewith he dispensed the wealth which rewarded his success. The Royal Society has good cause to cherish his memory as that of a genial Member who took an active interest in its affairs, affording it at all times the benefit of his business experience, and ever ready to aid financially any of its enterprises which seemed to him to stand in need of assistance. By his will also he has left a munificent benefaction whereby the Society will ultimately be enriched.

The other deceased Fellows on the Home List are Dr. Shelford Bidwell, Sir Robert Giffen, the Rev. Robert Harley, Mr. John B. N. Hennessey, Dr. Sydney Ringer, Mr. Edward Saunders, Sir Charles Todd, and Mr. C. Greville Williams.

The Report of the Council now presented to the Fellows contains a record of the main features of the work of the Society for the past year. To one or two parts of this work I wish to make brief allusion. It will be seen that, acting on the recommendation of the President and Council of the Society, the Government of this country has agreed to continue its subscription to the International Association of Seismology for six years more, up to the end of March, 1916. This prolongation of the adhesion of Great Britain is eminently desirable, in order that time may be allowed for the consideration of the best means of securing effective international co-operation in seismological observation and enquiry. In this branch of science our country has a special interest, for it was here that modern observational seismology was begun many years ago, and that the first network of observing and registering

seismological stations was established over the face of the globe. To the wide experience, great practical skill, and unwearied enthusiasm of our colleague, Dr. John Milne, the establishment and maintenance of that network of stations have been entirely due. With but little financial assistance from outside, he has borne the whole burden of the organisation, as well as of the voluminous correspondence which it entails with all parts of the world. The valuable service which he has thus rendered to the study of earthquakes has been universally recognised, and there is a widespread conviction that the system of observing stations which he has created is worthy of being made a national undertaking. The whole question of the future of seismology in this country must soon be seriously considered. Meanwhile, I would express my own personal hope that means will be found to place on a more permanent footing the work which Dr. Milne has originated and conducted, and to carry it on as successfully as in the past, but with an enlarged staff and more generous financial aid.

The Fellows are aware that for many years past the Society, at the request of different departments of Government, has undertaken the investigation of various diseases with the view of ascertaining their cause, and, if possible, of suggesting methods of treatment and cure. Chief among these enquiries is that of the appalling disease Sleeping Sickness. From the Report of the Council it will be seen that, although much important information has been obtained in Uganda, the investigation has had to be extended beyond the limits that originally seemed to be requisite, and that probably much still remains to be done before the conditions can be definitely stated in which trypanosome diseases are spread in tropical Africa. The work of those enquirers who are busy in London endeavouring to discover an effective drug for the treatment of trypanosomiasis is still in progress, with results which are so far encouraging for further investigation.

One of the most important statements in the Council's Report is that which has reference to the Gassiot Committee and the future of Kew Observatory. The arrangement therein detailed was the subject of long and careful enquiry and discussion. The Gassiot Committee has now been reconstituted and enlarged so as to make it an effective scientific body of advice in regard to magnetic, seismological or other geophysical observations which are to be conducted under the direction of the Meteorological Office.

Fellows of the Royal Society should be aware that they are divisible into two classes, those who were elected before 1878 and those who were elected after that year. The distinction is a pecuniary one. The older group paid £10 of entrance fee and an annual subscription of £4, which they still continue to pay. They are a dwindling band which now numbers only 57.

The second and younger group, by the institution of what is called the Fee-Reduction Fund, are relieved of the payment of an entrance fee and their annual contribution is reduced to £3, the remaining £1 being paid out of that Fund. When this arrangement was made it seems to have been calculated that the original capital sum of £10,111 5s. (which was raised by voluntary contributions), with the invested interest accruing from it, would yield an annual income of £600, which was estimated to be sufficient to meet the highest demand that was likely to be made on the Fund. But these calculations have proved erroneous, partly no doubt on account of the fall in the rate of interest and partly also because younger men have been elected into the Society than was formerly the case, so that the increase in the participators in the benefit of the Fund has not been balanced by deaths to the extent anticipated.

Consequently now, thirty years after the foundation of the Fund, the income, instead of amounting to £600 per annum, has only reached £467 4s. 9d. while the payments this year should be £474, viz., £150 in respect of fifteen entrance fees and £324 towards the annual contributions of 324 Fellows elected since 1878 and still living. There is, thus, this year, for the first time a deficit, which amounts to £6 15s. The excess of the sum which should be paid beyond the income of the Fund will increase annually, though at a diminishing rate, and will probably ultimately amount to about £50. It is obvious, therefore, that some new arrangement will require to be made. The Fellows elected since 1878 might be called upon to increase their annual subscriptions, but such a call would probably be felt to be both inconvenient and undesirable. An alternative would be to increase the capital of the Fund, and this would undoubtedly be the more acceptable solution of the difficulty. If the Treasurer could be put in possession of a sum of at least £1,000 he would be placed in a satisfactory position in regard to this portion of the Society's finances. So long as the deficit remains small the excess of income could be devoted to the increase of the capital, and consequently the sooner the sum required is obtained the better. I commend this matter to the consideration of the Fellows; among whom there are doubtless many who will be as glad to contribute substantial sums as were the original founders of the Fund.

MEDALLISTS, 1910.

COPLEY MEDAL.

The award of the Copley Medal has this year been made to one of our own countrymen, who has been more than fifty years a Fellow of the Royal

Society. Sir Francis Galton's life has been one of ceaseless activity in many varied departments of intellectual effort. Few of us can remember how he began as an enthusiastic explorer and geographer, "urged," as he confessed, "by an excessive fondness for a wild life," and with "the love of adventure" as his chief motive. He chose South Western Africa as the theatre of his exploration, penetrated into regions where no European foot had preceded him, and brought back with him a vivid impression of the scenery, physical geography, natural history, and ethnology of Damaraland and South Ovampoland. He embodied his observations in an interesting volume of travel published in 1853. That work showed that he was no mere hunter after game or seeker of adventure, but a shrewd and observant traveller, with his eyes open to every distinctive natural feature in the countries and their inhabitants. His experience in these African journeys led him to plan and to publish in 1854 his well-known and admirable hand-book, the "Art of Travel," which, as a pioneering treatise in the practical methods of scientific exploration, has proved of inestimable service to the travellers of the last half century.

Sir Francis at an early period of his career was led to interest himself in meteorology, which, as a science of observation, was then in its earliest infancy. With much labour and skill he constructed weather-charts, and discussed meteorological statistics. His zeal and success in these studies led to his being chosen a member of the Meteorological Council at its origin, and he remained in that position until the Council was superseded in 1901 by the Meteorological Office. He likewise acted as Chairman of the Royal Society's Committee of Management of Kew Observatory from 1888 till 1900, when the work of this Committee became merged in that of the National Physical Laboratory.

But it was not only in geography and meteorology that Sir Francis Galton manifested his versatile energies. He was much interested likewise in biological studies, especially in regard to questions of relationship and heredity. As far back as 1871 he began what has proved to be a voluminous and important series of contributions to these subjects. From his first paper, "Experiments in Pangenesis," down to his last volume on "Eugenics," his successive papers have shown a continuous development of ideas and conclusions. He was led from his early ethnological enquiries into the mental peculiarities of different races, to discuss the problems of Hereditary Genius, from the fundamental postulate that "a man's natural abilities are derived by inheritance under exactly the same limitations as are the form and physical features of the whole organic world." To obtain further data for the discussion of this subject, he carried out the elaborate statistical

enquiries embodied in his "English Men of Science." Confident in the results of these researches, he proceeded after the manner of "the surveyor of a new country who endeavours to fix in the first instance, as truly as he can, the position of several cardinal points." His results in this quest were given in his "Inquiries into Human Faculty and its Development," published in 1883. A further contribution was made by him in 1889, when his work on "Natural Inheritance" appeared. His subsequent papers and essays on "Eugenics" have still further stimulated enquiry into a subject of such deep interest and transcendent importance in all efforts to improve the physical and mental condition of the human race.

It has seemed to the Council fitting that a man who has devoted his life with unwearied enthusiasm to the study and improvement of many departments of natural knowledge, whose career has been distinguished by the singleness and breadth of its aims, and by the generosity with which he has sought to further them, should receive from the Royal Society its highest award in the Copley Medal.

RUMFORD MEDAL.

The Rumford Medal has been awarded to Prof. Heinrich Rubens in recognition of the value of his researches in radiation. For many years he has been engaged in the experimental investigation of optical radiations of very long wave-length. In the course of this work he elaborated, in conjunction with Prof. E. F. Nichols, a method of isolating pencils of nearly homogeneous rays, using the fact that a non-metallic substance reflects very copiously waves of the same length as those to which it is opaque. If then a pencil of rays of mixed wave-lengths is reflected several times to and fro between mirrors of the same kind of substance, the rays finally emerging (the "Reststrahlen") have the wave-lengths of the kinds of light which the substance refuses to transmit. The light of other wave-lengths has been transmitted freely at each incidence, and by a sufficient number of reflections is ultimately removed from the pencil. By using different substances as reflectors, Prof. Rubens has isolated infra-red light of various wave-lengths up to as much as 96μ , or about 0.1 of a millimetre; while, on the other hand, purely electric waves have been produced of wave-lengths as small as 2 millimetres. He has thus enormously extended our knowledge of the infra-red spectrum. Moreover, in conjunction with colleagues, he has investigated the absorbing and reflecting powers of substances for these long wave-length rays. He has shown that, for radiation of wave-length even less than ten times the wave-lengths in the visible spectrum, the reflecting and absorbing powers

of metals and alloys are determined by their electric conductivities alone, in accordance with Maxwell's theory. It followed from Maxwell's own observations on the absorption of gold-leaf for visible light that agencies more complex than conductivity must be involved for these shorter wave-lengths.

Prof. Rubens has recently applied to the measurement of the long infra-red wave-lengths a quartz interferometer, and among other results, he has found that the refractive index of water, for waves of length about 82μ , is of the same order as for waves in the visible spectrum, while for the shortest Hertzian waves yet examined, about 2000μ , it is as high as 9.

These examples will serve to illustrate how much Prof. Rubens has already done to bridge the gap between optical radiations and electric waves produced by direct electric agency, and how much more is to be expected from him in the investigation of the interval still remaining in which such fundamental changes of properties take place.

ROYAL MEDALS.

The awards of the two Royal Medals given annually by our Patron the King have received His Majesty's approval.

One of these Medals has been assigned to Prof. Frederick Orpen Bower in recognition of the great merit of his contributions to morphological botany, of which department of science he is the acknowledged leader in Great Britain. Prof. Bower's early studies in this field (1880—82), on the genera *Welwitschia* and *Gnetum*, were marked by the discovery of the true nature of the two persistent leaves in *Welwitschia*. The next period of his work was given to a study of the morphology of the leaf. He developed in 1884 the idea of the phyllopodium or leaf-axis, and discussed in 1885 the apex of the leaf in *Osmunda* and *Todea*. This latter study was cognate to subsequent researches, the results of which were given in 1886 in a review of "Apospory and Allied Phenomena." This work, of much intrinsic interest, is important as having led its author to formulate the views advanced in 1890 in a memoir on "Antithetic as distinguished from Homologous Alternation [of Generation] in Plants." Another memoir, published in 1889, on "The Comparative Examination of the Meristems of Ferns as a Phylogenetic Study," prepared in the light of the then received belief that the leptosporangiate ferns are the more primitive, was followed in 1891 by a discussion of this question in which Prof. Bower advanced morphological reasons for reversing the hitherto accepted phylogenetic order. The new conclusion has proved to be in accord with palæobotanical results, and marked another distinct step in the advancement of botanical science.

During the third period of his work, 1892—1903, Prof. Bower's papers, including an important series on the spore-producing members, have resourcefully maintained the antithetic doctrine, and have afforded a striking instance of the advantage of a well-considered working hypothesis as a guide to investigation. The career of morphological research here outlined has been recently crowned by the publication (1908) of a book on "The Origin of a Land Flora," which is one of the "most important contributions to the advancement of Natural Knowledge, published originally in His Majesty's dominions," within the period prescribed in respect of the award of Royal Medals.

The other Royal Medal has been adjudged to Prof. John Joly, who is eminent in two branches of science, geology and physics. This combination of studies has proved to be reciprocally fruitful to both departments. It was from his mineralogical interests that he was led to devise the steam calorimeter, which has enriched physics with an apparatus of high refinement. The use of this method was extended by him to the direct determination of the specific heats of gases at constant volume, a measurement dealing with minute quantities of heat under circumstances quite beyond the capabilities of the usual forms of calorimeter. Among many contributions to standard physical data, which are accepted and in use, may be instanced his determination of the density of saturation of steam. His meldometer, primarily intended for determining the melting points of mineralogical and geological specimens, has been the means of providing data for use in thermometry. He has devised and applied a method of determining the change of volume of rocks and other substances on fusion, which is a datum of primary importance for cosmical theories. He has carried out a refined research, with negative results, on the possibility of minute change of mass (as distinguished from weight) accompanying chemical combination. His recent extended investigations of the occurrence of radioactive substances in materials from various strata have been utilised for fundamental geological discussions. Of other useful inventions which he has introduced, one of the best known is the translucent block photometer.

Prof. Joly has made important contributions to the subject of colour photography, and devised some years ago a three-colour system in which all three colours are present on the same plate in the form of fine parallel lines or small dots.

He has also contributed substantially to the theory of biological processes, such as the ascent of sap in vegetation. Reference may likewise be made to his suggestive memoir on the Age of the Earth based upon a discussion of the chemical constitution of the Ocean.

DAVY MEDAL.

The Davy Medal has been assigned this year to Prof. Theodore W. Richards, as a mark of appreciation of the value of his work in the determination of the atomic weights of the elements. His researches on this subject have not been surpassed in comprehensiveness by those of any other chemist. He has himself determined the atomic weights of no less than 14 elements, and many other atomic weight determinations have been made under his direction and superintendence. The accuracy of the numbers obtained is certainly much higher than that which has been attained by any previous series of researches, and it is impossible to speak in too high terms of the ingenuity, the unremitting labour, and the masterly manipulation which Prof. Richards has brought to bear on his investigations.

In addition to this work on atomic weights, Prof. Richards has made many important contributions to physical chemistry, and it is probably no exaggeration to say that he has done more to raise the standard of accuracy in physico-chemical work than any other living chemist. Theoretical contributions to this branch of science are comprised in a series of papers on "The Possible Significance of Changing Atomic Volume," in which he suggests a relation between the energy of the atoms and their compressibilities. In order to test his hypothesis, he has made a long series of investigations on the compressibility of elements and compounds. He has determined this constant for nearly all the solid and liquid elements, and he has shown that the compressibility is a periodic function of the atomic weights. In electro-chemistry, Prof. Richards has made important determinations of the electro-chemical equivalent of silver, and he has supplied some of the most rigorous proofs of the universality of Faraday's Law.

DARWIN MEDAL.

To Mr. Roland Trimen, who was for many years Curator of the South African Museum, in Cape Town, the Darwin Medal has been awarded. His official position, and the duties it involved, enabled him to do admirable work in African zoology. His name will always stand with those of Bates and Wallace in the establishment and illustration of the theory of mimicry. In addition to his researches on that subject, he has done admirable systematic work, his descriptions of insects, especially the *Lepidoptera rhopalocera*, being models of accuracy and literary style. He, furthermore, rendered the greatest assistance to Charles Darwin, especially in his work on orchids—assistance the high value of which is acknowledged in a long series of that great naturalist's published letters.

SYLVESTER MEDAL.

The Medal which perpetuates the name and mathematical prowess of James Joseph Sylvester has this year been assigned to Dr. Henry Frederick Baker, in recognition of his work in the Theory of Functions, wherein he has shown himself to be a profound analyst. His book on the Abelian Functions, published in 1897, is a classic, and probably no better guide to the analytical development of pure mathematics has appeared during the last three-quarters of a century. While basing the argument of the work on the methods of Riemann, he never loses sight of the arithmetical ideas which we owe to Kronecker, Dedekind, and Weber, or of the geometrical notions brought to light by the labours of Clebsch, Gordan, Noether, and Klein. The critical insight which was thus in evidence marked him out a few years ago as the editor of Sylvester's Collected Papers. This work, which, with the approaching issue of the fourth and last volume, may be said to be complete, has been necessarily a difficult task, which besides making demands upon the resources of an accomplished mathematician has entailed no little editorial labour. Dr. Baker, by explanatory and critical observations, and by frequent ameliorations of the text, has done much to assist mathematical students. His scholarly work has resulted in a faithful record of the course of Sylvester's thought. It seems eminently fitting that the Sylvester Medal should be given to one who has erected so lasting a memorial to the great mathematician.

HUGHES MEDAL.

To Prof. John Ambrose Fleming the Hughes Medal has been awarded. For thirty years he has been actively engaged in researches in experimental physics, chiefly in the technical applications of electricity. He was an early investigator of the properties of the glow lamp, and elucidated the unilateral conductivity presented in its partial vacuum between glowing carbon and adjacent metal, a phenomenon which has been linked up recently with the important subject of the specific discharges of electrons by different materials. He has published in the scientific and technical press, and in technical textbooks, many admirable experimental investigations and valuable expositions in the applications of electricity, as, for example, to electric transformers and wireless telegraphy. Of special interest and value for theory were the important results concerning the alterations in the physical properties of matter, such as the remarkable increase in the electric conductivity of

metals, when subjected to very low temperatures, which flowed from his early collaboration with Sir James Dewar in investigating this domain. In recent years he has taken a prominent part in the scientific development of telegraphy by free electric waves.

Influence of Viscosity on the Stability of the Flow of Fluids.

By A. MALLOCK, F.R.S.

(Received October 10,—Read November 24, 1910.)

No part of the theory of hydrodynamics is more difficult than that relating to stability, and even were the conditions which determine the limits of stability thoroughly and satisfactorily investigated, only the fringe of the problem would be touched, for the chief interest in the cases presented by real fluids lies in the character of the motion after instability has been established.

In some restricted dynamical problems (*e.g.* an inverted pendulum) the system passes from an unstable to a stable configuration, and the whole process can be traced. With fluid motions, however, this is not the case, and there is no more prospect of tracing the course of a particle of fluid in an unstable flow than of following an individual molecule of gas in its various encounters with its neighbours.

Nevertheless, the direction and speed in a region of unstable flow is not in general a mere matter of chance, but rather one of periodic variation, though the periods involved are not in most cases definite, in the same sense as are the periods of stable systems, but are in character more nearly allied to the intervals which separate the times of activity of a geyser—intervals, that is, whose constancy depends on the uniformity of the rate at which energy is supplied or withdrawn from the fluid.

In all the streams, whether of gas or liquid, met with in nature, the conditions are in general those of instability, and it is only in certain cases, and by taking considerable precautions, that an approximately stable flow can be maintained, and where this is accomplished the stream-lines are of the electric type.

Although it is impossible by mathematical analysis to follow in detail the motion in an unstable flow, the general character may, in many cases, be traced, and the object of the present note is to apply an observation made by

the late Mr. Froude to the explanation of some of the commonly occurring phenomena of instability.

At the meeting of the British Association at Bristol in 1875, Froude showed,* among other experiments, one in which a jet issuing horizontally from an aperture in a vessel of water impinged symmetrically on a similar aperture in a vessel standing near the first (fig. 1). The water in the

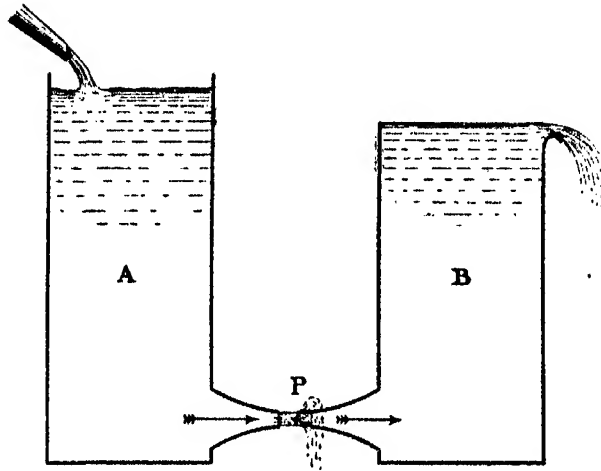


FIG. 1.

first vessel (A) was maintained at a uniform level, and by providing an outflow in the second vessel (B) at a slightly lower level, the stream from one to the other could be maintained indefinitely, nearly the whole of the outflow from A entering B at the speed due to the head. A small but definite loss of fluid, however, occurred at the entrance to the aperture in B, giving rise to the appearance shown at P in fig. 1. It will be seen that the loss is confined to a thin layer at the outer surface of the jet—to that part of the jet in fact which was in contact with or close to the walls of the passage from which it issued; and Froude pointed out that this was to be explained by the loss of velocity suffered by the outer part of the jet from surface friction and viscosity, for the fluid which has had its velocity lowered without having its pressure raised has had its potential degraded, and is therefore incapable of ever again entering a region where the pressure is greater than that due to its diminished velocity. The degradation of potential by viscous action gives the explanation of a very large number of natural phenomena, some of which are on a large scale, but before giving examples it

* Presidential Address to Section G.

will be convenient to examine the nature of viscous degradation more closely.

Suppose a stream of fluid flowing in a parallel channel with a velocity $v = \sqrt{2gH}$ (uniform over the whole section to begin with) has its velocity over a certain thickness near the walls reduced from v to θv by the action of surface friction and viscosity; the pressure is not altered in the layer, but the height to which its velocity can carry it is reduced from \sqrt{H} to $\sqrt{\theta H} = \sqrt{H'}$ so that $H'/H = \theta^2$. Now suppose the channel to contract; the stream-line pressure diminishes as the velocity increases, and there is nothing to prevent the degraded surface streams from retaining their surface position. If, however, the channel expands so as to make the stream-line pressure greater than H' , the degraded streams must have their onward flow diverted or reversed, and in either case the conditions of continuity will produce a change of flow in the central streams, different, not only in degree, but in kind, from any change due to the expansion of the electrical stream-lines.

Thus it will be seen that according to whether the electrical stream-lines are convergent or divergent, the results in the presence of viscous dissipation are of widely different characters. When the electrical stream-lines are convergent, the actual path of the retarded streams may be nearly the same as if viscosity were absent; but with divergent electrical flow this is impossible, if the divergency is such as to raise the pressure anywhere above that which is due to the speed of the degraded streams.

There is a difficulty in many real phenomena in distinguishing between the secondary currents arising from the conditions of continuity due to the diversion or reversal of the degraded streams, and the degraded streams themselves. Some sort of an eddy is necessarily formed, and although it would be too much to say that all eddies in real fluids are formed in this way, the following examples in which the explanation does apply will be sufficient to show how far-reaching the effect of degraded potential is, and how large what may be called the secondary effects of viscosity are, compared with those which appear in the initial stages of instability investigated by mathematicians:—

(1) It is well known that in many tidal waters (*e.g.* the English Channel) the stream continues to run in mid-channel after it has turned inshore. In this case the shallow water near the shore is more retarded than the mid-channel surface streams, and thus since the level of the water is not affected by viscous retardation, the degraded inshore stream is unable to hold up against the tidal gradient after this has reached some definite value (fig. 2, *a—f*). The same reasoning applies to all the fluid which is near enough to the boundary of the channel (whether bed or shore) to be sensibly

influenced by surface friction, and there can be no doubt that the tidal current along the bed of the channel is also reversed before that on the surface. In many tidal rivers this is known to be the case from actual observation.

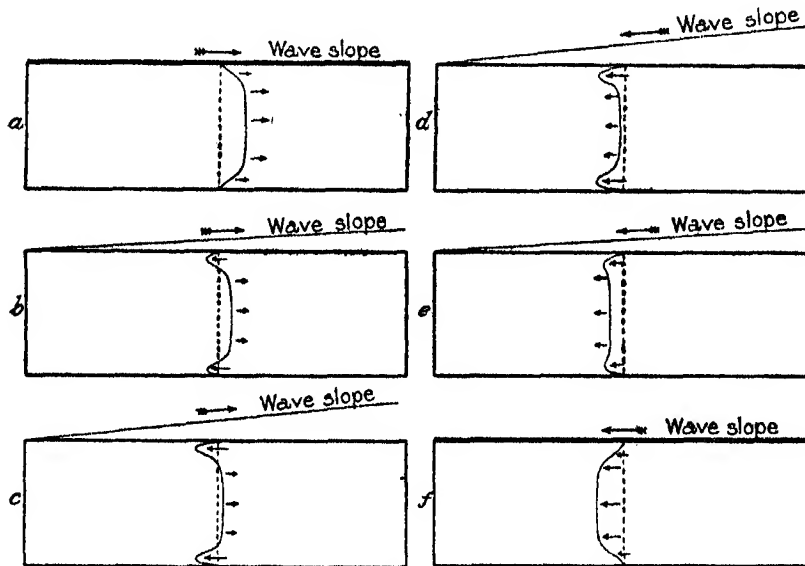


FIG. 2, *a—f*.—Diagrammatic plan of the direction of flow in a viscous fluid oscillating in a rectangular channel during one half period. *c* and *d* refer respectively to the times just before and just after the epoch of maximum wave slope.

(2) I have watched the same phenomenon in a canal under the following circumstances:—When a lock is being filled a stream is created in the canal, and as the lock fills this stream is gradually retarded and the water level at the lock rises in consequence above the mean level of the canal by an amount depending on the velocity of the stream (among other things). The stream in the canal is, of course, from the surface friction, slower at the sides than in the middle, and the side current there is reversed by the excess of head at the lock long before the central stream has ceased to flow in its primary direction. I have seen this reversal more than a quarter of a mile above a lock in a canal whose width did not exceed 30 feet.

The opposite directions of the side and central streams imply a vorticity in the fluid, and constitute together (including the reversal over the bed) a single long eddy. This is in itself unstable, and secondary eddies are formed along its length as in fig. 2, *g*. These, however, are generally difficult to observe, for the stream to begin with contains eddies of the same character, which tend to mix the layers at different distances from the

boundaries, and it is on this account the speed of rivers is more uniform over the cross-section than it would be were the flow lamellar.



FIG. 2, *g*.—Diagrammatic vertical section, showing the eddies in a current flowing in a rectangular channel.

(3) Another very typical case mentioned by Froude is the inward spiral motion which occurs near the bottom of a flat circular vessel while water rotating in it is coming to rest, which is made apparent by the way in which small objects are carried towards the centre.

Near the sides and floor the degraded streams are unable to describe plain circular orbits from lack of sufficient velocity to withstand the pressure due to the motion of the less retarded fluid, the result being that the centre of curvature of the orbit is shifted and the stream deflected inwards. The inward stream over the floor necessitates an upward central current and a slow outward flow at a higher level giving rise to a circulation such as is shown in fig. 3*a*.

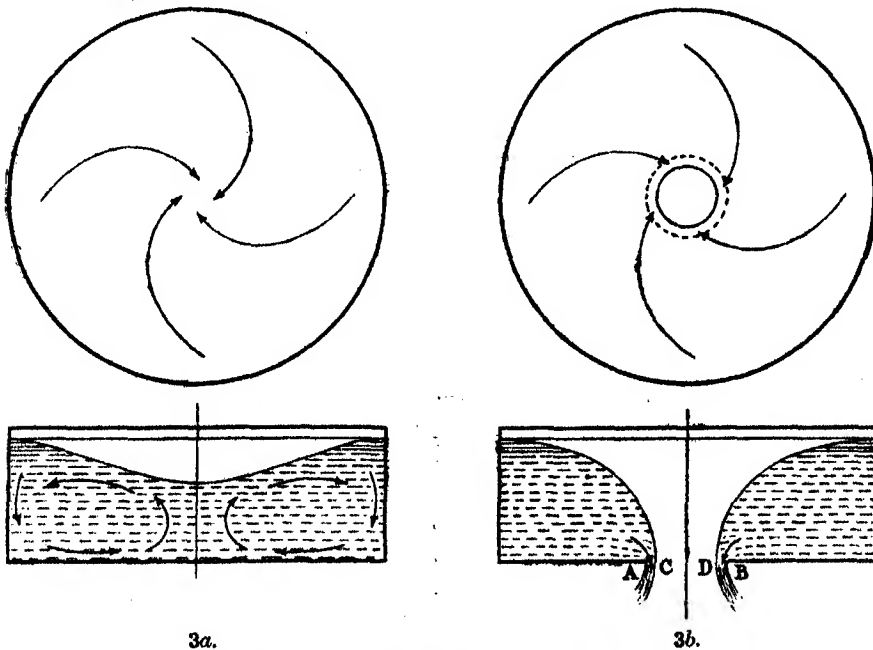


FIG. 3*a*.—Diagrams showing in plan the spiral current near the floor, and in section the vertical circulation set up when a viscous fluid which has been rotating in a circular vessel is being brought to rest by the action of the stationary boundaries.

FIG. 3*b*.—Plan and section of a vortex in a viscous fluid flowing from a central hole in a circular vessel.

The same phenomenon has been treated by Prof. James Thomson ('Roy. Soc. Proc.,' 1876), who explained in this way the formation of banks of gravel and pebbles which are found on the inside of the bends of quickly flowing rivers. In the slower tidal waters of estuaries the curious conformation of sand banks is a result of the same kind of action.

(4) As another example suppose fluid to be flowing from a circular hole in the floor of a large vessel in which the level at a distance from the outlet is maintained constant. If the fluid is without rotation the flow to begin with is purely radial. A flow of this character is unstable, and even the smallest angular velocity given to the mass will increase as the flow proceeds and ultimately the fluid itself will form a vortex, at the free surface of which the orbital velocity is that due to the difference of level between the point considered and the surface at a distance (fig. 3*b*). The effective area of the outlet is then determined by the difference of the diameters of the outlet and the tubular vortex surface at the floor level (viz., $AB-CD$ in the figure). If the liquid is devoid of viscosity $AB-CD = 0$ and the outflow ultimately ceases, but with a viscous fluid $AB-CD$ is always finite and the ultimate condition is reached when the energy in the fluid discharged is equal to the work expended in viscous dissipation within the vessel.

(5) Cases analogous to (3) and (4) occur in meteorology. The ordinary barometric depressions of large area may be considered as vortices undergoing viscous dissipation whose only store of energy is the kinetic energy due to velocity. These correspond to the circulation of liquid in a closed vessel as in example (3). The loss of velocity near the ground necessarily causes the degraded streams to turn inwards towards the centre, and the conditions of continuity demand that near the centre there must be an upward current.

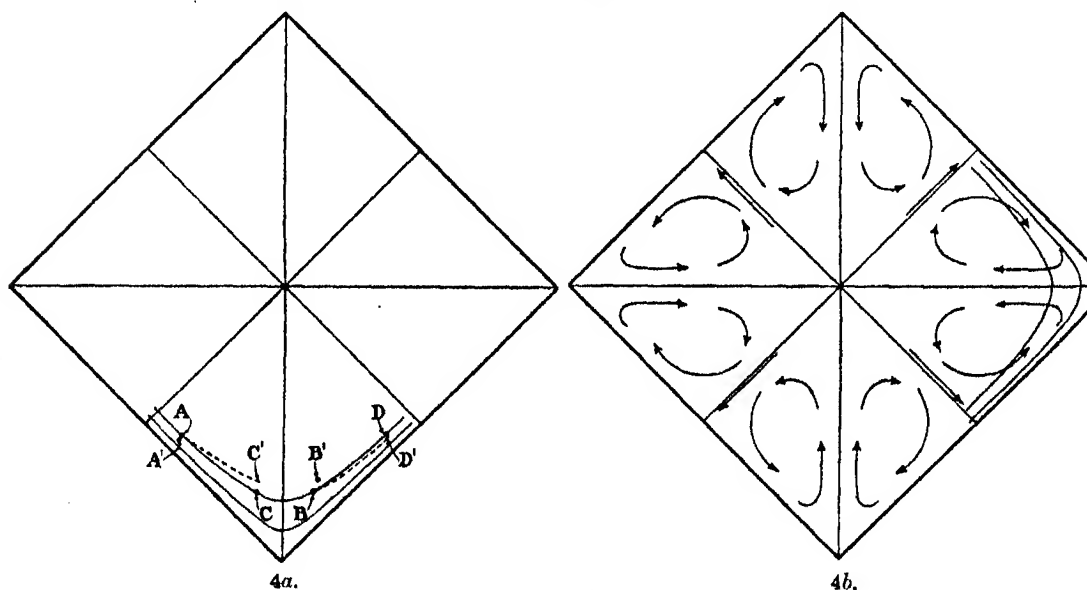
Whirlwinds, waterspouts, dust storms, and perhaps tornadoes have part of their energy in the potential form due to denser air lying for a time unstably over air which is lighter, and which when disturbed rushes up a chimney as it were of its own formation. These are analogous to (4). In both cases the inward slope of the spirals followed by the current depends on the amount of degradation which the stream has undergone; but for ordinary meteorological depressions the upward central current is a secondary effect of the degraded circulation, whilst in whirlwinds, etc., it is the primary cause.

(6) Similar considerations apply to slowly oscillating liquid. The simplest case is that in which the fluid completely fills a long prismatic box oscillating about an axis parallel to the edges of the prism.

The motion of the fluid far removed from the ends is then two-dimensional. The electric stream lines of the fluid in these circumstances are known, and it is not necessary for the present purpose to define them by symbols.

The relative velocity of the fluid and the solid boundary is a maximum through the planes parallel to the axis of rotation and passing normally through the middle of each side (if the prism is a regular polygon) and a minimum through the planes bisecting the angles. The general character of the flow is shown by the dotted lines in fig. 4a. In a perfect fluid the velocity and pressure are of course connected in the usual way.

If the fluid is viscous, consider the motion of two elements which start from A and B respectively and which in the absence of viscosity would follow the paths AC and BD. Here A moves from a region of low towards a region of higher pressure, while B travels from a higher towards a lower pressure.



FIGS. 4a and 4b.—Slow circulation set up in a viscous fluid completely filling a rectangular prismatic box oscillating about the axis of the prism. In Fig. 4a, A C B D is a stream line of perfect fluid referred to the boundary considered as stationary.

Owing to viscous retardation the paths AC' and BD' will both be shorter than AC and BD, but while there is no reason (except such as may be imposed by the conditions of continuity) that D' should not lie on BD, it is impossible that C' should lie on AC, for at all points along this path the pressure is greater than the head equivalent to the degraded velocity of the particle which starts from A. The actual path AC' must therefore lie inside and be more curved than AC. In the next quarter of an oscillation C' will return not to A but to A' outside A and D' to B' inside B.

The result of the first half of an oscillation is that a certain amount of

fluid will be carried inwards from the angles towards the centre of the prism and outwards from the centre towards the middle of the sides. The same process will go on in the succeeding half oscillation and if continued will give rise to a slow circulation such as is shown by the arrows in fig. 4*b*.

(7) An important case is that of the initiation of eddies in a stream flowing past an obstacle.

Let the obstacle be a lamina. As is well known there are two forms of mathematical solutions of this problem, one of which makes the stream-lines similar curves both up and down stream (electric flow) while the other involves a surface of discontinuity on the down stream side. As far as this portion of the flow is concerned, neither of the solutions represents even approximately what is observed to take place in real fluids, though the discontinuous form is not so far removed from the facts as is the electric flow. The form of the discontinuous surface of theory is determined by making its curvature such that, while fulfilling the conditions of continuity, the pressure just outside the surface and throughout the space within it is that of the fluid at a distance, the velocity just outside the boundary being that of the general stream and zero inside, fig. 5.

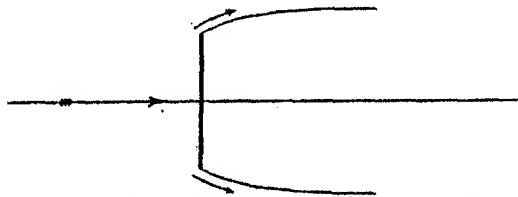


FIG. 5.—Discontinuous flow of a perfect fluid past a lamina at right angles to the stream.

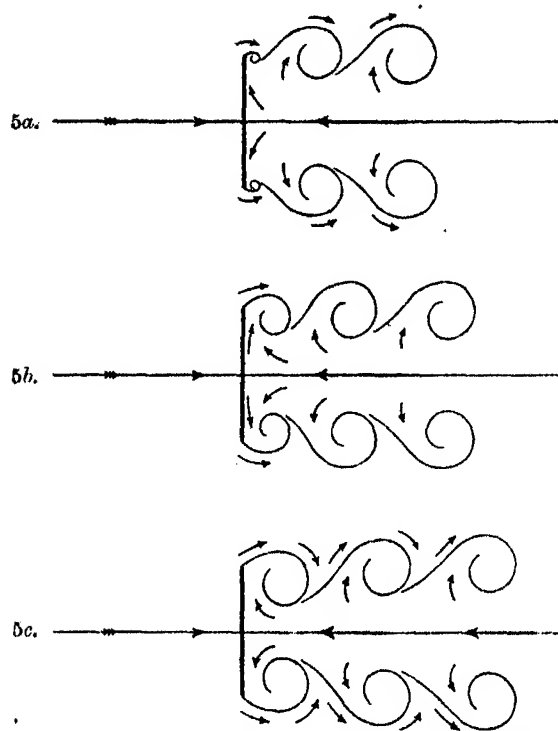
If the lamina were devoid of surface friction, and the liquid free from viscosity, this form of flow would be possible, though unstable.

In the actual case the fluid which is in contact with the up stream surface of the lamina is degraded and reaches the edge with a velocity insufficient to follow the theoretical curve. The result is that the fluid as it passes the edge is necessarily deflected inwards behind the down stream face of the lamina.

The subsequent motion cannot be followed by analysis. Observation, however, shows that the flow is not steady but of a periodic character, the actual period being determined by the velocity of the stream, the magnitude of lamina, and the angle between it and the general direction of flow.

Figs. 5*a*, 5*b*, 5*c* indicate the periodic structure of the wake in the case of a long lamina at right angles to the stream.

The inflow past the edge initiates a small eddy, about half of the fluid



FIGS. 5a, 5b, 5c.—Diagram illustrating the periodic formation of eddies in a viscous fluid under the same conditions as in Fig. 5.

involved being derived from the wake (or dead water behind the lamina) and half from the stream. The eddy continues to grow, and the conditions of continuity demand a current in the interior of the wake in the contrary direction to that of the outside stream to supply part of the fluid required for its formation. When the diameter of the eddy exceeds a certain fraction of the width of the lamina, the access of a sufficient supply from the central wake is impeded, and the full-grown eddy then leaves its position close to the lamina and travels down stream, while a fresh eddy is being formed in the same way at the edge. The general structure of the wake, therefore, consists not in a mass of dead water separated from the stream by a surface of discontinuity, but of a central current opposite to that of the stream bordered by a series of eddies at definite distances from one another.

It may be mentioned that the eddies just spoken of may be in the same state of growth at either edge, or be formed alternately (fig. 6). In the latter case the full-grown eddy occupies nearly the whole width of the lamina, and the wake consists of a trail of eddies alternately right-handed and left-handed.

How far the diameter of the full-grown eddy remains directly proportional to the width of the lamina it would be difficult to say. I have observed this proportionately up to a width of 20 cm., but would it be true when the width was as many kilometres? Under dynamically similar conditions it should be.

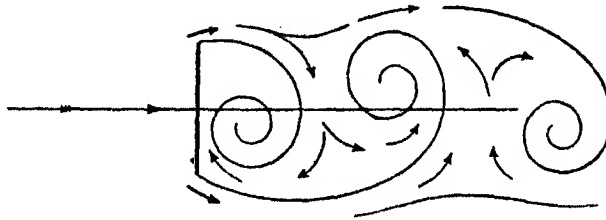


FIG. 6.—Diagram showing the alternate formation of right-handed and left-handed eddies in a viscous fluid.

(8) When the obstacle is not a lamina but a cylinder, the character of the wake is not greatly altered, and the eddies may be formed either simultaneously or alternately. In the alternate formation, the flow past the obstacle is more rapid round that side on which the eddy is growing than on the other, and the stream line pressure therefore less. Hence the force acting on the obstruction is not in the direction of the stream, but has a lateral component urging the obstruction towards that side.

(9) If the cylinder is a stretched string with a period of its own, and if the velocity of the stream is such that the period of eddy formation approaches the natural period of the string, it will be seen that the applied force is in the right phase to maintain a vibration when once started. This is the explanation of the action of the *Æolian* harp and many allied phenomena.

(10) The whistling of the wind is also a result of the periodic formation of eddies, but in this case the pitch of the note is in general dependent only on the velocity of the wind and the dimensions of the obstacle and not a coincidence of periods, and a sound will be produced whether the formation of the eddies is synchronous or alternate.

Many more examples might be given, but those already cited are sufficient to illustrate the far-reaching effects of the viscous degradation of potential, and of the principle to which Froude called attention, as explaining the difference in the behaviour of a viscous fluid, according to whether the motion is towards regions of increasing or diminishing pressure.

*Optical Dispersion : An Analysis of its Actual Dependence upon
Physical Conditions.*

By T. H. HAVELOCK, M.A., D.Sc., Armstrong College, Newcastle-on-Tyne.

(Communicated by Prof. Sir Joseph Larmor, Sec. R.S. Received October 10,—

Read November 24, 1910.)

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1. *Introduction.*

The influence of a transparent medium upon light passing through it may be ascribed to two factors ; one is the existence, in each individual molecule or particle, of vibrating parts with certain natural frequencies, and the other is the physical condition of the aggregation of molecules composing the medium. Suppose that a typical vibrating part is an electrified particle of charge e and mass m , whose free vibrations are given by equations of the type

$$m \frac{d^2x}{dt^2} + fx = 0. \quad (1)$$

Let X be the corresponding component of electric force in the incident light wave. The impressed force, to be supplied on the right-hand side of (1) for the actual motion, is not simply eX , but has an additional term to express the effect of the surrounding molecules ; the simplest conception of this effect indicates a term directly proportional to the average polarisation P of the surrounding molecules at each instant. Hence, instead of (1), we have an equation

$$m \frac{d^2x}{dt^2} + fx = e(X + \sigma P_x). \quad (2)$$

As regards the numerical value of the co-efficient σ , little can be said beforehand on theoretical grounds; certain considerations, given in the present connection by Lorentz and by Larmor, indicate that for gases and liquids σ should be approximately $\frac{1}{3}$.

The following investigation is an attempt to extract from available experimental data, information about the numerical value of σ and its variation with changing physical conditions. The problems concerned are those of optical dispersion in isotropic and æolotropic media, and the changes produced by varying density, pressure and temperature, or by the action of external electric or magnetic fields. No attempt is made to explain the intimate mechanism of these phenomena, that is, the physical process by which the value of σ is altered; rather, the term is used as a possible means for including the various effects under one formal scheme, at least for a first approximation. The method is, in fact, analogous to the usual procedure of describing absorption effects by introducing a term in dx/dt into equation (2), without thereby specifying completely the physical process involved in absorption.

If we ignore the effect of surrounding molecules in equation (2), that is, if we put σ zero, the dispersion formula which can be deduced is of the type

$$n^2 - 1 = \sum_s \frac{C_s}{\lambda^2 - \lambda_s^2}, \quad (3)$$

where n is the refractive index of the medium for wave-length λ , C_s is a constant associated with the vibrating electrons of type s , and is proportional to the number of such per unit volume, λ_s is the wave-length corresponding to the natural frequency of the same type, and the summation Σ extends over all the types. Again, if we put σ equal to $\frac{1}{3}$, we obtain a dispersion formula

$$\frac{n^2 - 1}{n^2 + 2} = \sum_s \frac{C_s}{\lambda^2 - \lambda_s^2} \quad (4)$$

In both cases, if we assume the quantities C_s to be proportional to the density ρ , and divide either of equations (3) and (4) by ρ , we obtain on the right-hand side a quantity dependent only upon the constitution of the individual molecule; the expression on the other side must also be independent of the physical conditions of the aggregation. In this way two relations connecting refractive index and density have arisen, namely

$$\frac{n^2 - 1}{\rho} = \text{constant}; \quad \frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \text{constant}. \quad (5)$$

These relations have been the subject of numerous investigations. The

second one gives generally a better agreement with the facts, especially in cases of change of state from vapour to liquid; however, when the refractive indices at different temperatures and under different pressures are compared, it is found that neither relation expresses all the facts; these cannot be ascribed merely to change of density.

We might then fall back upon simply asserting that the quantities C_s and λ_s in (3) or (4) must vary with the physical conditions, or, in other words, the natural frequencies of the individual molecules must be affected by pressure, temperature, or external action on the medium; for a small variation one would obtain from (3) a dispersion formula

$$2n \, dn = \sum_s \left\{ \frac{dC_s}{\lambda^2 - \lambda_s^2} + \frac{2C_s \lambda_s d\lambda_s}{(\lambda^2 - \lambda_s^2)^2} \right\}. \quad (5)$$

This in fact has generally been the procedure in previous investigations. In contrast to this method, we shall consider here to what extent the facts can be expressed in terms of two variables, the density ρ and the quantity σ , without introducing changes in the inherent molecular frequencies.

It has been remarked that the cause of the disagreement between the second relation in (5) and experiment must be looked for partly in the fact that σ is not exactly equal to $\frac{1}{2}$, partly also in changes that take place in the interior of the particles when a body is heated or compressed; these changes causing a variation in the value of the coefficients f in equation (2).^{*} Without denying that both these are probably true contributing causes, it seems of interest to examine separately the former supposition, especially as it has been ignored in favour of the latter as sole cause.

2. *Refractive Index and Physical Conditions.*

If we retain the quantity σ we can deduce a dispersion formula like (4) but with $(n^2 - 1)/\{1 + \sigma(n^2 - 1)\}$ on the left hand side. The coefficients C_s are proportional to the number of vibrating parts of given type in unit volume; if we make the usual assumption that they are proportional to the density and if we divide through by ρ , we have

$$\frac{n^2 - 1}{1 + \sigma(n^2 - 1)} \frac{1}{\rho} = \sum \frac{C_s}{\lambda^2 - \lambda_s^2}. \quad (6)$$

On the right hand we have now, by supposition, a function of the wave-length λ and the constitution of the individual particle; hence for a given wave-length and for all physical conditions of the aggregation of particles, we should have

$$\frac{n^2 - 1}{1 + \sigma(n^2 - 1)} \frac{1}{\rho} = \text{const.} \quad (7)$$

^{*} H. A. Lorentz, 'The Theory of Electrons,' p. 147.

It may be noted that if we divide throughout by σ we may write this relation as

$$\frac{n^2-1}{n^2+a} \frac{1}{\rho} = \text{const.} \quad (8)$$

This has been used as a generalised form of (5); but it clearly ignores the dependence of σ upon the physical conditions, and has in fact been no more successful than the simpler relation.

The formula in (7) may be put more conveniently as

$$\rho \left(\sigma + \frac{1}{n^2-1} \right) = \text{const.} \quad (9)$$

Now we have no means of calculating σ independently, so this relation cannot be verified directly. To obtain numerical values of σ we shall have to fix its value in some standard condition; before doing so, we can deduce a difference-equation which can be put to the test of experiment. If the suffixes 1 and 2 denote values in two different states of a medium composed of similar individual particles we have

$$\rho_1 \left(\sigma_1 + \frac{1}{n_1^2-1} \right) = \rho_2 \left(\sigma_2 + \frac{1}{n_2^2-1} \right).$$

Hence
$$\frac{\rho_2}{n_2^2-1} - \frac{\rho_1}{n_1^2-1} = \rho_1 \sigma_1 - \rho_2 \sigma_2 = C. \quad (10)$$

Thus, for two physical states, the difference in $\rho/(n^2-1)$ is constant for all wave-lengths; by supposition σ is independent of the wave-length, hence the left-hand side of (10) is a function only of physical conditions such as temperature, pressure, density, and so forth. The two relations given previously in (5) are special cases of (10) given by $\sigma_1 = \sigma_2 = 0$ and $\sigma_1 = \sigma_2 = \frac{1}{2}$; so that if either of the formulæ (5) held, the constant in (10) would have the value zero or $\frac{1}{2}(\rho_1 - \rho_2)$ respectively.

Two special forms of (10) for small changes should be noted, that is, when it may be written $d\{\rho/(n^2-1)\} = \text{constant}$.

First, if the pressure is constant and the temperature t is the independent variable, we have

$$\frac{\alpha}{n^2-1} + \frac{2n}{(n^2-1)^2} \frac{dn}{dt} = \text{const.}, \quad (11)$$

where $\alpha = -d(\log \rho)/dt = \text{coefficient of cubical expansion}$.

Secondly, if the temperature is constant and the pressure p varies,

$$\frac{\beta}{n^2-1} - \frac{2n}{(n^2-1)^2} \frac{dn}{dp} = \text{const.}, \quad (12)$$

where $\beta = d(\log \rho)/dp = \text{coefficient of compressibility}$.

From (11) we have

$$\frac{dn}{dt} = C_1 \frac{(n^2-1)^2}{2n} - \alpha \frac{n^2-1}{2n}. \quad (13)$$

Thus if C_1 is a positive quantity it is possible for the temperature variation dn/dt to change sign from positive to negative; this would occur for a wave-length at which the index of refraction equals $\sqrt{1+\alpha/C_1}$.

We shall examine now the relations (10), (11), and (12). Where special reference is not made, the data used have been taken from Landolt and Börnstein ('*Physikalisch-Chemische Tabellen*') or from Winkelmann ('*Handbuch der Physik*').

3. *Temperature Variation: Organic Liquids.*

A preliminary comparison may be made by using a set of liquid organic compounds which have been examined in a similar manner by Voigt*; the data are taken from the collection in his paper. Voigt adopts the hypothesis that thermal or mechanical deformation produces a change in the natural frequencies of the vibrations within the molecule in addition to the effect due merely to the change of density; he gives expression to this change by tabulating for different wave-lengths the values of a quantity T defined by

$$\frac{n_1^2-1}{\rho_1} - \frac{n_2^2-1}{\rho_2} = \frac{(\rho_1-\rho_2)T}{\rho_1\rho_2}. \quad (14)$$

Apart from a few exceptions, due probably to inaccurate data, Voigt finds that for liquids T is positive and increases regularly with decreasing wave-length. Now if we compare (14) with (10) we see that C is equal to $T(\rho_1-\rho_2)/[(n_1^2-1)(n_2^2-1)]$; it is possible then for C to remain constant for different wave-lengths since, in general, n_1 and n_2 increase with decreasing wave-length.

Table I shows the results of the calculations for the heat expansion of nine liquids, namely, those used by Voigt as a random selection from available data; in each case the mean value of C , that is of $\rho_2/(n_2^2-1) - \rho_1/(n_1^2-1)$, is compared with the value of $\frac{1}{8}(\rho_1-\rho_2)$, so that one sees the divergence from the simpler Lorentz formula.

One may say that the general result of these calculations is favourable to the relation given in (10); such divergences as occur are irregular in character, and are probably due in these cases to insufficient accuracy of the values of density and refractive index. Without laying too much stress on the actual numerical values, it appears that C may be considered constant within the range of wave-lengths concerned in each case.

* W. Voigt, '*Annalen der Physik*' (4), 1901, vol. 6, p. 459.

More recent experiments are available in the case of water and carbon disulphide and we shall examine these now.

Table I.

Aniline.—12°—28°. Mean $C = 0.00280$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00455$.					
λ	691	656	589	486	434
$10^5 C$	256	294	269	289	290
Acetylene dibromide.—15°—25°. Mean $C = 0.00516$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00750$.					
λ	656	589	486	397	
$10^5 C$	517	525	518	502	
Ethyl alcohol.—0°—20°. Mean $C = 0.00410$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00563$.					
λ	656	589	486	397	
$10^5 C$	413	406	407	415	
Ethylene bromide.—15°—25°. Mean $C = 0.00534$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00758$.					
λ	656	589	486	397	
$10^5 C$	536	533	524	543	
Benzene.—12°—28°. Mean $C = 0.00425$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00545$.					
λ	691	656	589	486	434
$10^5 C$	428	412	481	395	409
Iodobenzene.—7°—22.2°. Mean $C = 0.00224$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00790$.					
λ	760	589	486	397	
$10^5 C$	268	294	208	129	
Methylacetate.—16°—24°. Mean $C = 0.00058$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00319$.					
λ	656	589	486	434	
$10^5 C$	57	55	60	61	
Thiophene.—16°—24°. Mean $C = 0.0004$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.0033$.					
λ	656	589	486	434	
$10^5 C$	34	56	45	24	
Vinyl tribromide.—15°—25°. Mean $C = 0.00479$; $\frac{1}{3}(\rho_1 - \rho_2) = 0.00733$.					
λ	656	589	486	434	
$10^5 C$	470	471	476	500	

4. Carbon Disulphide and Water.

Flatow* has examined in detail the dispersion of water and carbon disulphide, measuring the absolute refractive index at various wave-lengths, and for several different temperatures; he concludes that the Lorentz relation $(n^2 - 1)/(n^2 + 2)\rho = \text{const.}$ is approximately satisfied, and he has also calculated for each temperature a dispersion formula of the type

$$n^2 = m + \frac{m'\lambda^2}{\lambda^2 - \lambda'^2} - k\lambda^2,$$

in order to study the variation of λ' with the temperature. We shall consider dispersion formulæ in a later section; at present we use Flatow's experimental results to test the relation (10).

* E. Flatow, 'Annalen der Physik' (4), 1903, vol. 12, p. 85.

Carbon disulphide.—We have measurements of n at nine wave-lengths for the temperatures -10° , 0° , 20° , and 40° . The densities have been calculated from the known expansion of CS_2 , and with the value $\rho_0 = 1.2931$. We are able in this way to form three sets of differences; using the notation

$$C_0^{20} = \left(\frac{\rho}{n^2 - 1} \right)_{20^\circ} - \left(\frac{\rho}{n^2 - 1} \right)_{0^\circ},$$

the results are shown in Table II.

Table II.—Carbon Disulphide.

λ .	$10^5 C_0^{-10}$.	$10^5 C_0^{20}$.	$10^5 C_{20}^{40}$.
274	327	676	657
361	310	583	639
394	288	595	668
441	266	594	678
467	263	598	685
480	253	593	642
508	253	604	635
533	256	609	645
589	274	617	639

Comparing mean values of C and the changes in density, we have the following:—

$$C_0^{-10} = 0.00274; \quad C_0^{20} = 0.00607; \quad C_{20}^{40} = 0.00649;$$

$$\frac{1}{3}(\rho_{-10} - \rho_0) = 0.0049; \quad \frac{1}{3}(\rho_0 - \rho_{20}) = 0.0099; \quad \frac{1}{3}(\rho_{20} - \rho_{40}) = 0.0103.$$

As regards the constancy of C , the results may be regarded as satisfactory, considering the order of accuracy that may be expected. Considerable deviations occur at the two smaller wave-lengths (0.274μ and 0.361μ). It must be remembered that here we approach the dominating region of absorption in the ultra-violet, which is in the neighbourhood of 0.225μ ; and it is known that also a minor region of absorption occurs between these two values, near 0.325μ , which is sufficient to cause slight anomalies in the refractive index.* In the relation (10) absorption has not been taken directly into account, so deviations may be expected as one approaches a region of absorption.

* W. Fricke, 'Annalen der Physik,' 1903, vol. 16, p. 865.

Another way of expressing these results is by using the alternative form (11), the changes being small and the pressure constant; thus approximately

$$C_0^{20} = 20 \frac{d}{dt} \left(\frac{\rho}{n^2-1} \right)_{10^\circ}, \quad \frac{C_0^{20}}{20\rho_{10}} = -\frac{\alpha}{n^2-1} - \frac{2n}{(n^2-1)^2} \frac{dn}{dt}.$$

Using the mean value of C_0^{20} we find the rate of change of n at 10° given by

$$\frac{dn}{dt} = -0.001162 \frac{(n^2-1)}{2n} - 0.000238 \frac{(n^2-1)^2}{2n}. \quad (15)$$

In this case we notice that dn/dt remains negative for all wave-lengths. Graphing dn/dt with respect to λ from (15) we obtain practically the same curves as that given by Flatow as the result of his experiments; in the visible region dn/dt varies only slowly, but in the ultra-violet it diminishes very rapidly algebraically with decreasing wave-length. As regards variation with the temperature, it should be noted that both the numerical coefficients in (15) would be slightly different for other temperatures.

Water.—We have observations at five temperatures, 0° , 20° , 40° , 60° , and 80° ; using the same range of wave-lengths, and with the same notation, we have the results in Table III.

Table III.—Water.

λ .	$10^4 C_0^{20}$.	$10^4 C_{20}^{40}$.	$10^4 C_{40}^{60}$.	$10^4 C_{60}^{80}$.
274	191	233	310	313
308	188	252	343	350
340	190	261	363	369
361	198	259	366	378
394	188	276	377	385
441	186	282	385	400
480	170	264	384	410
533	165	268	385	404
589	159	267	400	394

From these we have for mean values and difference of densities:

$$\begin{aligned} C_0^{20} &= 0.00181; & C_{20}^{40} &= 0.00263; \\ \frac{1}{3}(\rho_0 - \rho_{20}) &= 0.00055; & \frac{1}{3}(\rho_{20} - \rho_{40}) &= 0.00230; \\ C_{40}^{60} &= 0.00368; & C_{60}^{80} &= 0.00378; \\ \frac{1}{3}(\rho_{40} - \rho_{60}) &= 0.00301; & \frac{1}{3}(\rho_{60} - \rho_{80}) &= 0.00380. \end{aligned}$$

It cannot be said that the results are very satisfactory when analysed in this manner. On the other hand there is nothing decisive against the present theory; for if C_0^{20} has a slight regular decrease, C_{40}^{60} and C_{80}^{80} increase a little with increasing wave-length, while C_{20}^{40} is irregular. Further, if we make the calculations for the smallest wave-length used (0.214μ), we find small values for the four quantities, viz., $C_0^{20} = 0.00148$; $C_{20}^{40} = 0.00150$; $C_{40}^{60} = 0.00216$; $C_{80}^{80} = 0.00185$. Flatow himself, in calculating dispersion formulæ, found greater deviations for wave-lengths between 0.217 and 0.267μ ; owing to these appearing at all the temperatures, he concludes that they are not due to experimental inaccuracies, but possibly to a neglected region of absorption.

Another point in which water is peculiar in the present connection is the occurrence of a minimum density in the region considered; as regards the constancy of $(n^2 - 1)/(\kappa^2 + 2)\rho$, we see from the comparison of C_0^{20} and $\frac{1}{2}(\rho_0 - \rho_{20})$ that this fact makes a considerable divergence in this region.

Taking the observations and calculations for water as they stand, one concludes that, although the results allow of the present interpretation, the evidence is more doubtful in character than for other substances examined.

5. *Organic Liquids.*

Falk* has investigated in great detail the variation of refractive index with temperature for a series of liquid organic compounds, using the sodium line (D_1) and the three hydrogen lines (C, F, and G'); the density of each liquid was also determined at various temperatures. It was found that within the limits of experimental error, both the refractive index for given wave-length and the density were linear functions of the temperature. For five temperatures ranging from 10° to 80° , Falk calculated, for the four wave-lengths, the quantities $(n-1)/\rho$, $(\kappa^2-1)/\rho$, and $(\kappa^2-1)/(\kappa^2+2)\rho$; each of these quantities shows for a given wave-length a small, but regular and continuous, change with the temperature, either increase or decrease. The quantity a was also calculated, so as to give the best average results for the relation $(\kappa^2-1)/(\kappa^2+a)\rho = \text{constant}$, for each liquid. For the present purpose, the data for the two extreme temperatures, 10° and 80° , have been used to calculate C_{10}^{80} , the difference in value of $\rho/(\kappa^2-1)$ for the two temperatures for each wave-length; the results are shown in Table IV.

The only substances which show regular variation in the values of C_{10}^{80} are nitrobenzene and monomethylaniline. It is stated that owing to the colour of the liquid the G' line (434) was too indistinct for measurements

* K. G. Falk, 'Journ. Amer. Chem. Soc.,' 1909, vol. 31, p. 86 and p. 806.

Table IV.—Values of $10^4 C_{10}^{80}$.

Wave-length	656.	589.	486.	434.	Mean.	$\frac{1}{3}(\rho_{10}-\rho_{80}) \cdot 10^4$.
Diisomyl	112	113	116	107	112	180
Dimethylaniline	110	107	109	112	109	193
<i>n</i> -Heptyl alcohol	104	90	107	101	100	166
Benzyl alcohol	138	130	134	133	134	175
<i>n</i> -Butyric acid	104	90	88	90	93	230
Acetylacetone	282	288	315	302	297	223
Isobutyl acetate	187	129	136	140	136	246
Ethyl <i>n</i> -butyrate	141	140	130	136	137	250
Isomyl acetate	141	130	134	126	133	228
Methylhexyl ketone	97	95	90	96	94	200
Nitrobenzene	122	127	128	—	126	230
Monomethylaniline	105	107	126	—	113	189
Benzyl cyanide.....	93	94	94	93	94	190
Benzaldehyde	99	92	95	104	98	207

to be made in these two cases; thus the regular increase seems clearly to be connected with exceptional absorption. For all the other substances it can at least be said that there is no regular increase or decrease of C with decreasing wave-length, so that it is permissible to regard the variations as accidental. In the previous section we noticed that Voigt has measured the effect of temperature by the change in $(n^2-1)/\rho$, and found that this change increased regularly with decreasing wave-length in general. The same remark applies to the present collection of liquids, with one or two doubtful cases; however, in about six cases the regular increase is broken by the quantity being greater for the C line than for the D line. The effect of this can be noticed in the column (656) in the table above. For instance, if we calculate the difference in value of $(n^2-1)/\rho$ at 10° and 80° for benzyl alcohol for the four wave-lengths, we obtain the sequence 0.0229, 0.0220, 0.0240, and 0.0251. This might possibly indicate some experimental error for observations with the C line; if not, it seems a curious effect. The mean values in column 5 of Table IV are equal to the mean values of $\sigma_{10}\rho_{10}-\sigma_{80}\rho_{80}$, from relation (10). We cannot as yet calculate absolute values for σ , but the numbers C_{10}^{80} measure the rate of increase of $\sigma\rho$ with temperature. The

large value of 0.0297 for acetyl acetone may be noticed; according to Falk, this substance is exceptional in the above collection, owing to its being a tautomeric mixture of two forms, the relative proportions changing with the temperature. Another point is that the isomeric substances, isobutyl acetate and ethyl *n*-butyrate have practically the same rate of change for the product $\sigma\rho$.

6. Pressure Variation.

As regards the change of refractive index n with pressure p , experimental data are not so numerous for liquids; at least not in a form suitable for the present analysis, for which observations are needed at various wave-lengths. In order to illustrate the alternative formula (12), a set of observations on carbon disulphide is taken from a paper by Röntgen and Zehnder.* The data are the values of dn/dp for the B, D, and F lines, the compressibility $\beta = 89.5 \times 10^{-6}$, and the index $n = 1.6297$ for the sodium line. From the values for the sodium line we calculate the value of C in relation (12) and obtain thus

$$10^6 \frac{dn}{dp} = 89.5 \frac{n^2 - 1}{2n} + 22 \frac{(n^2 - 1)^2}{2n}. \quad (16)$$

Estimating the values of n for the other two lines we can calculate from this equation the values of dn/dp . The results are shown in the following Table V:—

Table V.—Carbon Disulphide.

λ .	$10^6 \frac{dn}{dp}$, obs.	$10^6 \frac{dn}{dp}$, calc.
687	62.2	62.1
589	63.9	63.9
486	67.4	66.7

7. Artificial Double Refraction in Liquids.

In previous papers† the present scheme was developed in a simple form in connection with artificial double refraction produced by mechanical strain or by the action of an electric or magnetic field. The formal basis of the theory is the supposition that the effects can be represented by an anisotropic change in the quantity σ . If the density remains constant and if the

* W. C. Röntgen and L. Zehnder, 'Annalen der Physik,' 1891, vol. 44, p. 24.

† 'Roy. Soc. Proc.,' A, vol. 80, p. 28, 1907; also 'Phys. Rev.,' 1909, vol. 28, p. 136.

medium becomes doubly refracting like a uniaxal crystal with n_1 and n_2 for principal refractive indices, the relation (10) becomes

$$\frac{1}{n_1^2 - 1} - \frac{1}{n_2^2 - 1} = \text{constant.} \quad (17)$$

If the changes are small, with n the refractive index for the isotropic medium at same density, we have

$$\frac{n \, dn}{(n^2 - 1)^2} = \text{constant.} \quad (18)$$

This relation has been confirmed by recent researches, at least as a first approximation for the double refraction induced in liquids by an electric or magnetic field; reference may be made to the experimental and theoretical investigations of McComb,* Skinner,† Cotton and Mouton,‡ and Natanson.§

Although the present aim is rather to include various phenomena within a single formal scheme than to analyse in detail the physical mechanism of each effect, a few remarks may be made in the present instance. All the relations such as (10), (17), and (18) have been developed by considering the medium as effectively an assemblage of optically isotropic particles; all the changes which occur in the dispersion, whether isotropic or ceolotropic, are expressed in terms of two variables: the density ρ and the quantity σ . In the previous work quoted above the physical process was conceived of as a rearrangement of the particles in space. Cotton and Mouton prefer to regard it as an orientation of anisotropic molecules, and they give a theoretical deduction of relations (17) and (18) which is said to rest on this hypothesis.|| Now this assumption is possibly preferable for certain physical reasons, but it is not clear where it enters into the proof referred to above. In fact the proof is formally the same as ours, in that it ascribes the birefracton to a directional variation in the quantity σ ; the hypothesis of orientation enters in the assertion that it is the cause of these changes in σ , and of course if the particles are to orientate under a field of force they must be in some way anisotropic. Perhaps one might reconcile the hypothesis of orientation and the theoretical proof of relation (17) by considering the particles as in some way physically anisotropic but optically isotropic, just as one might regard for instance the particles of a crystalline substance which is optically isotropic; then one might have the possibility

* H. E. McComb, 'Phys. Rev.', 1909, vol. 29, p. 525.

† C. Skinner, 'Phys. Rev.', 1909, vol. 29, p. 541.

‡ A. Cotton and H. Mouton, 'Ann. de Chim. et de Phys.', 1910, vol. 19, p. 153.

§ L. Natanson, 'Bull. de l'Acad. des Sciences, Cracovie,' June, 1910.

|| Cotton and Mouton, *loc. cit. ante*, p. 217.

of orientation without interfering with the simplicity of isotropy in the optical equations.

If we wish to consider the particles as optically anisotropic, and the isotropy of the medium to be the result of averaging due to all possible orientations, we should have the following scheme. The equations of motion of a typical electron take, instead of (2), the form

$$\begin{aligned} m \frac{d^2x}{dt^2} + f_x x &= e(X + \alpha P_x), \\ m \frac{d^2y}{dt^2} + f_y y &= e(Y + \beta P_y), \\ m \frac{d^2z}{dt^2} + f_z z &= e(Z + \gamma P_z). \end{aligned} \quad (19)$$

Suppose now the extreme case when all the particles are orientated the same way; then we should have a crystalline medium with three principal refractive indices n_1 , n_2 , and n_3 given by the equations

$$\begin{aligned} \left(\sigma_1 + \frac{1}{n_1^2 - 1} \right)^{-1} &= \Sigma \frac{C_{n1}}{\lambda^2 - \lambda_{n1}^2}, \\ \left(\sigma_2 + \frac{1}{n_2^2 - 1} \right)^{-1} &= \Sigma \frac{C_{n2}}{\lambda^2 - \lambda_{n2}^2}, \\ \left(\sigma_3 + \frac{1}{n_3^2 - 1} \right)^{-1} &= \Sigma \frac{C_{n3}}{\lambda^2 - \lambda_{n3}^2}. \end{aligned} \quad (20)$$

On the other hand, if the particles are arranged at random in all possible directions, we should have an isotropic medium of index n_0 , for which we could write

$$\left(\sigma_0 + \frac{1}{n_0^2 - 1} \right)^{-1} = \Sigma \frac{C_n}{\lambda^2 - \lambda_n^2}. \quad (21)$$

In general, if we admit optical anisotropy of the particles, this in itself would contribute directly to the observed double refraction, as well as indirectly through the alteration in the σ -quantities.

One hypothesis would be to ignore the quantities σ , or make them all equal; this would ascribe the doubly-refracting properties to the differences between λ_n , λ_{n1} , λ_{n2} , and λ_{n3} . But the relation between these quantities does not seem obvious, except that the right-hand side of (21) is in some way an average of those in (20).

Another hypothesis, one by which the simple relations (17) and (18) are obtained, is to regard the right-hand sides of equations (20) and (21) as all the same function of the wave-length λ ; that is, we do, in effect, treat the molecules as if they were *optically* isotropic.

Cotton and Mouton have also investigated the variation of the induced

double refraction with the temperature; they find that in general the diminution is greater with increase of temperature than could be accounted for by the mere change of density. This result was involved in one case in the calculation given by the present writer for carbon disulphide;* expressing the results of Blackwell in the form

$$dn = C \frac{(n^2 - 1)^2}{n},$$

it was found that $C = 4.36 \times 10^{-7}$ at 11° and $C = 4.26 \times 10^{-7}$ at 24° .

So that, although the change in n is allowed for, there is in addition a decrease in C . With the present notation C is $\frac{1}{2}d\sigma$, and if we take the average decrease between the two temperatures we have

$$d(d\sigma)/dt = -1.55 \times 10^{-9}.$$

It might be possible to connect this with the rate of change of σ with the temperature for the isotropic medium; but it would doubtless be necessary to examine in more detail the physical nature of the changes which occur.

[Since the above remarks were written, a preliminary note has been published by Langevin,† dealing with the theory of electric and magnetic double refraction from the point of view of molecular orientation; the note records the results obtained. Apparently the molecule is supposed to be anisotropic, but account is taken of differences between electric, magnetic, and optical asymmetry; the action of the external field is, to modify the distribution of the molecular axes in space. As regards the dispersion, it is stated that the relation (18) above is obtained under certain conditions.]

8. *Temperature Variation in Solids.*

Although one expects more complexity in the case of solid substances, it seems of interest to express the experimental results by the same method as for liquids. It has been well established that the effect of temperature on the dispersion of solids is not merely due to the change of density, and it is here especially that recourse has been had to dispersion formulæ showing changes in the natural resonance-frequencies.

Glass.—The extensive researches of Pulfrich‡ are available, and we choose three examples which have already been examined by Voigt. The following Table VI shows the results :—

* *Loc. cit. ante*, p. 35.

† P. Langevin, 'Comptes Rendus,' August 16, 1910.

‡ C. Pulfrich, 'Annalen der Physik,' 1892, vol. 45, p. 609.

Table VI.

λ	656	589	486	434
S 57. Heavy Flint Glass, $\alpha = 2.804 \times 10^{-5}$.				
n	1.9491	1.9625	1.9979	2.0803
$10^6 dn$	1.204	1.447	2.090	2.810
T	-4.471	-4.876	-5.976	-7.190
$10^6 C$	1.60	1.68	1.86	2.07
O 527. Light Flint Glass, $\alpha = 2.696 \times 10^{-5}$.				
n	1.5389	1.5718	1.6529	1.7187
$10^6 dn$	-0.008	+0.014	+0.080	+0.187
T	-1.359	-1.488	-1.831	-2.127
$10^6 C$	1.95	1.85	1.64	1.50
S 40. Crown Glass, $\alpha = 2.613 \times 10^{-5}$.				
n	1.5366	1.5619	1.6211	1.6680
$10^6 dn$	-0.814	-0.805	-0.246	-0.287
T	-0.992	-1.075	-1.323	-1.505
$10^6 C$	1.40	1.35	1.30	1.22

In the above table, T is the quantity calculated by Voigt in the manner referred to previously (§3); for small changes the relation is

$$T = -\frac{2n}{\alpha} dn - (n^2 - 1),$$

where α is the cubical coefficient of expansion.

Also the quantity C of the present theory is given by

$$C = \frac{2n dn}{(n^2 - 1)^2} + \frac{\alpha}{n^2 - 1} = -\frac{\alpha}{(n^2 - 1)^2} T.$$

It appears that T is negative and increases numerically with decreasing wave-length. For the heavy glass S 57, the increase in the factor $(n^2 - 1)^2$ is not sufficient to counteract the increase in T, and the quantity C shows a regular increase; in the other two glasses the effect is the other way and C shows a regular decrease in the same direction.

One must remember that glass is not a simple substance but is a complex mixture, a fact which is illustrated by its optical behaviour under mechanical stress. Further, Pulfrich considered that the observed changes in refractive index were connected with a variation of absorption in the ultra-violet region; Königsberger* has also observed in solid bodies a displacement of this absorption region towards the longer wave-lengths with rising temperature. The direct influence of absorption has not been taken into

* J. Königsberger, 'Annalen der Physik,' 1901, vol. 4, p. 796.

account in the present theory, so that one cannot say how the results would be modified thereby.

Meantime, it appears that the variation of the σ -quantity must play a considerable part in a complete theory of the phenomena. Similar general remarks apply to the following calculations, which are tabulated here for comparison.

Amorphous Quartz.—Observations on this substance have been made by Martens;* the wave-lengths range from $0.185\ \mu$ to $0.508\ \mu$. With the usual notation the following Table VII shows the results for some of the wave-lengths. If the substance were the same as fused quartz or silica it would have a very small coefficient of expansion; whether this was the case or not, it appears that if we take α to have the mean value for quartz (0.000036), the values of C show a remarkable constancy in this range. If we calculate the values of T as before, we find it varies regularly from -1.969 at $508\ \mu\mu$ to -3.510 at $185\ \mu\mu$. We notice that dn/dt is positive in this range. If we take the mean value of C to be 55×10^{-6} , and if we assume C to remain constant, we can calculate when dn/dt would become negative; it would be zero when $n^2 - 1 = \alpha/C$, that is, when $n = 1.287$ approximately. As n is 1.575 at $185\ \mu\mu$ and 1.457 at $656\ \mu\mu$, the wave-length in question would be large; judging from the refractive index of ordinary quartz, it might be in the neighbourhood of $5\ \mu$ or $6\ \mu$, approaching a region of absorption in the infra-red.

Table VII.—Amorphous Quartz.

λ .	$10^6 \frac{dn}{dt}$	$10^6 C$.	λ .	$10^6 \frac{dn}{dt}$.	$10^6 C$.
185	2.319	57.6	298	1.225	54.2
193	2.080	56.5	346	1.141	54.4
206	1.832	55.7	361	1.127	54.6
214	1.728	55.5	441	1.041	54.4
226	1.590	55.0	480	1.020	54.3
257	1.374	54.4	508	1.021	54.7
274	1.301	54.3			

Fluor Spar and Rock Salt.—Micheli† has observed the variation of dn/dt for several substances, with wave-lengths ranging from about $185\ \mu\mu$ to $589\ \mu\mu$.

* F. F. Martens, 'Berichte der Deutsch. Phys. Ges.', 1904, p. 308.

† F. J. Micheli, 'Annalen der Physik,' 1903, vol. 7, p. 772.

All the curves obtained by graphing dn/dt against λ show a rise towards smaller values of λ . The most striking result is that for rock salt, where dn/dt varies from $+2.987$ at $202\ \mu\mu$ to -3.747 at $643\ \mu\mu$. If we calculate the quantity C in this case, we find that it varies only slowly in the visible region, having a value of about 28×10^{-6} , but increases rapidly in the ultra-violet. If we use the value 28×10^{-6} to calculate where dn/dt changes sign, and estimate the wave-length from a dispersion formula, we obtain the position as $175\ \mu\mu$; the experimental curve cuts the axis at about $220\ \mu\mu$. Similar remarks apply to the calculations for fluor spar, where C has a value of about 24×10^{-6} in the visible region, but rises rapidly in the ultra-violet to 37×10^{-6} at $185\ \mu\mu$.

In the case of solids such as those examined above, we find that if we use the value of C in the visible region to calculate a curve for dn/dt , the curve so obtained falls below the experimental curve when the latter begins to vary rapidly in the ultra-violet.

It is unnecessary to add further calculations of the same type, or one might examine data available from experiments on elastic deformation of solids, or from the double refraction of natural crystals and its variation with temperature and pressure—probably with similar results. The general conclusion is that the variation of the quantity σ needs to be considered in each case, but the changes in solids are too complex to be brought under a simple scheme with only two or three variables.

9. *Change from Vapour to Liquid.*

In this region the relation $(n^2 - 1)/(n^2 + 2)\rho$ has had its greatest success compared with the other simple formulæ. Calculations for many substances have been given by Brühl;* from his data we calculate the quantity C the present theory for six typical substances, including those for which the Lorentz formula shows most disagreement. Two wave-lengths are given, the Li and Na lines; the data for the vapours are for a temperature of about 100° , while the liquids vary between 10° and 20° . Table VIII shows the values of C , the differences between values of $\rho/(n^2 - 1)$ for vapour and liquid, for the two wave-lengths; the agreement between the second and third columns is as good as could be expected. The values of $\frac{1}{3}(\rho_l - \rho_v)$ are given for comparison.

* Brühl, 'Zeitschrift für Phys. Chem.,' 1891, vol. 7, p. 1.

Table VIII.—Values of $C_{\text{liquid}}^{\text{vapour}}$.

λ	Li.	Na.	$\frac{1}{2}(\rho_l - \rho_v)$.	σ_l .
Carbon disulphide.....	0·3911	0·3907	0·4200	0·3094
Chloroform	0·4942	0·4952	0·5015	0·3276
Ethyl alcohol.....	0·2564	0·2565	0·2653	0·3214
Methyl alcohol	0·2671	0·2685	0·2645	0·3367
Propyl iodide.....	0·7524	0·7521	0·5775	0·4323
Benzene	0·3196	0·3209	0·2922	0·3639

10. *Absolute Values of σ .*

We have so far been concerned only with a difference equation, the quantity C_2^1 being equal to $\rho_2\sigma_2 - \rho_1\sigma_1$; thus we obtain a relation between the values of σ in two different states. If we wish to assign numerical values to σ , we must fix its value in some standard state. At first it might be thought advisable to follow the ordinary theory, and make σ equal to $\frac{1}{2}$ in the gaseous state. If we try this for carbon disulphide we can calculate from Table VIII the value of σ for liquid CS_2 at 10° : knowing the densities of the vapour and liquid, and putting $C_2^1 = 0\cdot391$, we obtain thus $\sigma_l = 0\cdot3104$. This is less than the value of σ in the gaseous state; but σ represents the additional force on a particle due to the surrounding molecules, so it seems preferable that σ should be greater for a substance in the liquid state than when gaseous. This result can be obtained by making σ very small for gases; this is allowable, as, owing to the small values of $n-1$, there is no evidence to decide between the degree of constancy of the various forms $(n-1)/\rho$, $(n^2-1)/\rho$ or $(n^2-1)/(n^2+2)\rho$.

To make the matter definite, we may decide provisionally to make σ zero for gases, and for simplicity we fix the standard state as the gaseous condition supposed to be at 0° and a pressure of 760 mm. With this assumption, the values of σ in the last column of Table VIII have been calculated. One cannot deduce much from the values, as the data for gases are possibly not very accurate and the liquids are at various temperatures; otherwise it might be of interest to trace, for instance, a connection between the values of σ and the chemical constitution of the substance. It may be noticed that the "specific refraction" is $1/\{\sigma + 1/(n^2-1)\}\rho$; thus, for example, the large value of σ for propyl iodide would give a corresponding divergence in the specific refraction ordinarily used. On the present scheme, anomalies in

molecular refraction might be ascribed, in part, at least, to the indirect effect of intra-molecular action specified by the σ -quantity.

Air.—Magri* has made observations on the refractive index of air at high densities; he found that $(n^2-1)/(n^2+2)\rho$ gave the best approach to constancy. In Table IX some of his results have been used to calculate σ ; in the column under σ_0 are the values under the assumption that σ is zero in the standard state, while under $\sigma_{\frac{1}{2}}$ are the values if σ is $\frac{1}{2}$ in that state. The column $\frac{1}{3}(1-\rho_0/\rho)$ shows the value which σ should have in each case in order that $(n^2-1)/(n^2+2)\rho$ should have always its value for unit density; the last column gives the actual value of this quantity referred to unit density at 0° C. The temperature for the first row is 0° C, while for the other cases it varies between 14°·3 and 14°·9. Assuming the experimental data to be sufficiently accurate, the variations both in σ and σ_0 are curious, σ_0 rising to a minimum with increasing density, and then falling to approximately $\frac{1}{3}$. It may be noticed how an apparently large difference between σ_0 and $\frac{1}{3}(1-\rho_0/\rho)$ makes little change in the values in the last column. The results given here are referred to later in § 12.

Table IX.—Air.

Density.	σ_0 .	$\sigma_{\frac{1}{2}}$.	$\frac{1}{3}\left(1-\frac{\rho_0}{\rho}\right)$.	$\frac{n^2-1}{(n^2+2)\rho} 10^7$.
1	0	0·3333	0	1953
14·84	0·004	0·0224	0·3109	1947
42·13	0·4715	0·4794	0·3254	1959
69·24	0·4363	0·4411	0·3285	1961
96·16	0·4030	0·4065	0·3299	1961
123·04	0·3549	0·3576	0·3306	1956
149·53	0·3495	0·3517	0·3311	1956
176·27	0·3352	0·3371	0·3314	1953

Carbon Disulphide.—By combining the observations of Flatow, referred to previously, with values of n for the vapour, we can see how the value of σ varies with temperature and density. For the vapour, we know n for one wave-length of the series used for the liquid, viz., the line 589 $\mu\mu$. If we use the data $\rho = 0\cdot00342$, $n = 1\cdot00148$, and $\sigma = 0$ for the vapour, together with $\rho = 1\cdot2931$ and $n = 1\cdot64411$ for the liquid at 0°, we find

* L. Magri, 'Physikalische Zeitschrift,' 1905, vol. 6, p. 629.

$\sigma = 0.3069$. Using this value for all wave-lengths at 0° , we can calculate the values for various wave-lengths at 20° and 40° ; the results for four cases are contained in Table X. There is a small regular increase in σ with rise in temperature, although the density diminishes.

Table X.—Values of σ for CS_2 ; $\sigma_0 = 0.3069$.

λ .	20° .	40° .
274	0.3087	0.3112
441	0.3094	0.3117
508	0.3093	0.3119
589	0.3092	0.3118
Mean	0.3091	0.3116

Water.—For the vapour we use $\rho = 0.000809$, $\sigma = 0$, and $n = 1.00025$ for sodium light. Carrying out similar calculations, we find the following series of mean values of σ for the liquid:—

0° .	20° .	40° .	60° .	80° .
0.3362	0.3350	0.3344	0.33361	0.33364

It is of interest to compare with these some values for ice, which is a uniaxial crystal; Pulfrich has measured the two indices n_0 and n_e for various wave-lengths. Let σ_0 and σ_e be the corresponding principal values of σ for ice at 0° ; with the density $\rho' = 0.91674$, the following table shows the values of $\rho'/(n_0^2 - 1) - \rho'/(n_e^2 - 1)$ for certain wave-lengths, using absolute values of the indices:—

	Ice.			
λ	760	670	589	485
C_e^0	0.00625	0.00632	0.00608	0.00628

Now for water at 0° , and at wave-length 589, we have $\rho/(n^2 - 1) = 1.28174$; thus, if σ_w is the value for water at 0° , we have the equations

$$\rho'(\sigma_e - \sigma_0) = 0.00608 = C_e^0,$$

$$\rho\sigma_w - \rho'\sigma_0 = 0.00079 = C_w^0,$$

$$\rho'\sigma_e - \rho\sigma_w = 0.00529 = C_e^w,$$

From these, with $\sigma_w = 0.3362$, we find $\sigma_0 = 0.3660$ and $\sigma_e = 0.3726$. The actual numbers would probably be modified with more information with which to compare them; however, it appears that in the change to the solid state σ is increased.

11. *Dispersion Formulae: Absorption Maxima.*

It would seem possible to obtain values of σ by constructing dispersion formulæ of a suitable type; before examining a few cases it is necessary to consider certain points in regard to the wave-lengths for which absorption is a maximum. The argument may be given first for a simple formula, such as

$$n^2 - 1 = \sum_i \frac{C_i}{\lambda^2 - \lambda_i^2}. \quad (22)$$

Consider the values of n in the neighbourhood of a "resonance" wave-length, say λ_1 ; suppose that this is sufficiently isolated so that we may take the other terms in (22) as constant, that is, we write

$$n^2 = q_1 + \frac{C_1}{\lambda^2 - \lambda_1^2}. \quad (23)$$

From this equation n^2 is negative, and consequently n imaginary, for the range of wave-length given by $(\lambda_1^2 - c_1/q_1)^{\frac{1}{2}} < \lambda < \lambda_1$. If in (23) we regard n as complex and equal to $n(1 - i\kappa)$ we should have $n\kappa$ zero, except within the above range, where it increases from zero at the lower limit to infinity at the upper limit λ_1 . This effect is, of course, not a true absorption effect, but would mean that the medium refused to admit certain radiation within a definite range of wave-length. If we now insert a term in the equations of the medium to represent absorption, we have instead of (23), an equation

$$n^2(1 - i\kappa)^2 = q_1 + \frac{C_1}{\lambda^2 - \lambda_1^2 + i\beta_1\lambda}. \quad (24)$$

Following the method used by Lorentz* for a similar equation with q_1 equal to unity, we write the last term of (24) as $c_1/(\alpha + i\beta)$; then we have

$$n^2(1 - \kappa^2) = q_1 + \frac{C_1\alpha}{\alpha^2 + \beta^2}; \quad 2n^2\kappa = \frac{C_1\beta}{\alpha^2 + \beta^2}. \quad (25)$$

Solving these, we obtain

$$\begin{aligned} 2n^2 &= \sqrt{q_1^2 + \frac{C_1^2 + 2q_1C_1\alpha}{\alpha^2 + \beta^2}} + q_1 + \frac{C_1\alpha}{\alpha^2 + \beta^2}, \\ 2n^2\kappa^2 &= \sqrt{q_1^2 + \frac{C_1^2 + 2q_1C_1\alpha}{\alpha^2 + \beta^2}} - q_1 - \frac{C_1\alpha}{\alpha^2 + \beta^2}. \end{aligned} \quad (26)$$

If we assume, further, the usual simplification, viz., that β is large, we obtain finally the approximate result

$$n\kappa = \frac{C_1\beta}{2q_1^{\frac{1}{2}}(\alpha^2 + \beta^2)}. \quad (27)$$

* H. A. Lorentz, 'The Theory of Electrons,' p. 310.

Thus the retention of q_1 does not affect the form of the result, and the deduction follows that the maximum of $n\kappa$ is in the neighbourhood of $\alpha = 0$, that is, of the wave-length λ_1 .

Returning to the dispersion formula (22), the previous argument is of the type which has been relied on when the quantities λ_s have been identified with absorption maxima observed experimentally; as far as the simple formula is concerned, these quantities are the upper limits of the ranges in which n is imaginary and are the wave-lengths for which n^2 is infinite.

If we turn now to the type of formula used in the previous work, we have

$$\frac{1}{\sigma + 1/(n^2 - 1)} \frac{1}{\rho} = \Sigma \frac{C_s}{\lambda^2 - \lambda_s^2}. \quad (28)$$

In the neighbourhood of λ_1 we have now

$$\frac{1}{\sigma + 1/(n^2 - 1)} \frac{1}{\rho} = q_1 + \frac{C_1}{\lambda^2 - \lambda_1^2}. \quad (29)$$

If we solve this for n^2 we find

$$n^2 = q_1' + \frac{C_1'}{\lambda^2 - \lambda_1'^2}, \quad (30)$$

with $q_1' = \frac{1 + q_1\rho(1 - \sigma)}{1 - q_1\rho\sigma}; \quad C_1' = \frac{C_1\rho}{(1 - q_1\rho\sigma)^2};$

$$\lambda_1'^2 = \lambda_1^2 + \frac{C_1\rho\sigma}{1 - q_1\rho\sigma}.$$

The lower limit for which n is imaginary is equal to

$$\sqrt{(\lambda_1'^2 - C_1'/q_1')} = \left\{ \lambda_1^2 - \frac{C_1\rho(1 - \sigma)}{1 + q_1\rho(1 - \sigma)} \right\}^{\frac{1}{2}},$$

while the upper limit is

$$\lambda_1' = \left\{ \lambda_1^2 + \frac{C_1\rho\sigma}{1 - q_1\rho\sigma} \right\}^{\frac{1}{2}}. \quad (31)$$

Thus both the limits of the range of imaginary values for n are altered by the introduction of the quantity σ , a fact which was noticed by Larmor* in discussing optical dispersion. It is clear that if we introduce a term representing true absorption, the argument would follow the same lines from equation (30) as from equation (23); consequently, we are led to identify the absorption maximum with the upper limit of the above range in (31). With a dispersion formula of type (28), the quantities λ_s represent true "resonance" wave-lengths belonging to the individual atom or molecule; it is not permissible to identify them with maxima of absorption, or selective reflection, which have been determined experimentally for the medium as a whole. To

* J. Larmor, 'Phil. Trans.,' A, 1897, vol. 190, p. 240.

determine the latter, in any case, we must write the dispersion formula as in (29), and the wave-length required is $\{\lambda_1^2 + C_1\rho\sigma/(1 - q_1\rho\sigma)\}^\frac{1}{2}$, instead of λ_1 .

Numerical illustrations may be taken from two cases, where a dispersion formula of the type (28) has been used without taking account of this change.

Carbon Disulphide.—In the paper already quoted, Flatow has calculated dispersion formulæ of the type

$$n^2 = m + \frac{n'\lambda^2}{\lambda^2 - \lambda'^2} - k\lambda^2$$

for CS_2 at various temperatures; he finds λ' to be about 0.227μ , varying slightly with the temperature. There is a region of absorption ranging from 0.190μ to 0.228μ with a maximum at 0.210μ approximately; there is also a minor region of absorption near 0.325μ . By a method of continued reflection, Flatow found a maximum at 0.231μ and concludes that the value of 0.227μ for λ' agrees well with this for a natural frequency. He also states that a dispersion formula of the Lorentz-Planck type gives a value of 0.185μ for λ' , and consequently gives a worse agreement than the older form. In the latter calculation Flatow ignores the effect considered above, and also uses a specially simple type of formula, viz. $(n^2 - 1)/(n^2 + 2) = g\lambda^2/(\lambda^2 - \lambda'^2)$. But for carbon disulphide we must use at least a three-constant formula. Suppose, for comparison, we assume that σ is $\frac{1}{2}$, and make the calculations with

$$\frac{n^2 - 1}{n^2 + 2} = q + \frac{C_1}{\lambda^2 - \lambda_1^2}$$

determining the constants from the data

λ	441	508	589
n	1.67180	1.64586	1.62806

With sufficient approximation for the purpose we find the values

$$q = 0.33567, \quad C_1 = 0.005843, \quad \lambda_1^2 = 0.04338.$$

Thus we find λ' is 0.208μ . But this is not to be compared with the experimental data; according to the previous argument, the quantity to be so used is $\sqrt{\{\lambda_1^2 + C_1/(1 - q)\}}$ in the present notation. Working this out for the above values we find the value 0.228μ , giving practically the same agreement as the older formula.

Rock Salt and Fluorite.—Following Larmor's development of the present type of dispersion formula, to which reference was made above, Maclaurin* has deduced and illustrated the form

$$\frac{n^2 - 1}{n^2 + a} = \sum \frac{C_s}{\lambda^2 - \lambda_s^2}. \quad (32)$$

* R. C. Maclaurin, 'Roy. Soc. Proc.,' A, 1906, vol. 81, p. 367.

For a given physical state of the medium this form is equivalent to (28) above, with a equal to $(1-\sigma)/\sigma$; however, the previous form is preferable when we wish to consider changes of dispersion for changing physical conditions, and it also enables us to separate out a quantity independent of these conditions.

Maclaurin gives numerical calculations for two substances, rock salt and fluorite; identifying $n(\infty)$ with the dielectric constant K , he uses (32) in the form

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{C_1}{\lambda^2-\lambda_1^2} + \frac{C_2}{\lambda^2-\lambda_2^2}. \quad (33)$$

A very close agreement is shown between calculated and observed values of n over a large range of wave-length; in addition Maclaurin claims that K , λ_1 , and λ_2 agree with the mean values of the best experimental data. However, the quantities λ_1 and λ_2 are identified directly with the observed maxima of absorption or reflexion; we calculate now what difference is made by the argument of the present section, using Maclaurin's values of the constants for the dispersion formula (33).

For rock salt we have—

$$\begin{aligned} \lambda_1^2 &= 0.0160074, & \lambda_2^2 &= 2632.14, \\ C_1 &= 0.00191605, & C_2 &= 683.816, \\ a &= 5.51, & K &= 5.9, \\ \lambda_1 &= 0.12652 \mu, & \lambda_2 &= 51.3 \mu. \end{aligned}$$

Putting λ_1 for λ in the last term of (33), we have, in the vicinity of λ_1 ,

$$\frac{n^2-1}{n^2+5.51} = q' + \frac{C_1}{\lambda^2-\lambda_1^2}, \quad \text{with } q' = 0.169652.$$

Hence the required wave-length is given by $\sqrt{\{\lambda_1^2 + C_1/(1-q')\}}$, that is, 0.1353μ . The lower limit of the range for which n is imaginary is $\sqrt{\{\lambda_1^2 - aC_1/(1+aq')\}}$ or 0.1027μ . We have seen that it is the upper limit which, consistently with the similar argument for the simpler dispersion formula, should be identified with the experimental data.

For the neighbourhood of λ_2 we find $q' = 0.429449$ and the result is that n is imaginary between 38.9μ and 61.9μ ; hence if we use the numerical values given above it is 61.9μ that should be compared with experiment instead of 51.3μ .

We may compare with this Paschen's formula for rock salt of the Sellmeier type;* this gives a natural wave-length of 60μ in the infra-red and in its neighbourhood we have $n^2 = 5.680142 + 12059.95/(\lambda^2 - 3600)$. We find then that n is imaginary between approximately 38.4μ and 60μ ; the upper limit

* F. Paschen, 'Annalen der Physik,' 1908, vol. 26, p. 130.

being compared with the absorption maximum, although Paschen regards it as an open question how far the observed "Reststrahlen" maxima can be identified with the wave-lengths of the natural vibrations which dominate the dispersion in the infra-red.

A smaller value of the constant a would probably give a better agreement in this respect. In fact Maclaurin states that he tried at first a equal to 2; he found then a fair agreement between calculated and observed values of n , but with the values of λ_1 and λ_2 as much below the observed values as they were above them with an ordinary Sellmeier dispersion formula.

As regards dispersion formulæ in general, it should be remembered that we replace the actual substance by an ideal simplified medium with only two or three natural frequencies; it may happen that the actual substance has two or three very predominant regions of resonance, in which case there should be good agreement between calculated and observed positions for these. On the other hand it may be that there are two or three regions of equal value not far apart, and the calculated value would be a mean position. For instance, recent observations on rock salt show maxima at 46.9μ and 53.6μ .* It appears that the quality of the agreement between observed and calculated values of refractive index even over a considerable range is not sufficient in itself to decide between different hypotheses, and for instance to give reliable values of a or σ .

In respect to the absorption regions in the infra-red, the dispersion often gives no more than a single term $-k\lambda^2$, which we could make up from any number of places of selective absorption in the absence of further information; numerical values are obtained only when we assume the definite simplification of a small number of natural frequencies and use the value of the dielectric constant.

For fluorite Maclaurin gives the following values:—

$$\begin{array}{ll} \lambda_1^2 = 0.00716764, & \lambda_2^2 = 576.353, \\ C_1 = 0.001303, & C_2 = 231.856, \\ a = 1.04, & K = 6.8, \\ \lambda_1 = 0.0846618 \mu, & \lambda_2 = 24.0074 \mu. \end{array}$$

With the same notation as before, we find in the neighbourhood of λ_1 that $q' = 0.337497$; hence $\sqrt{\{\lambda_1^2 + C_1/(1-q')\}} = 0.09557 \mu$. Also near λ_2 we have $q' = 0.739785$, and $\sqrt{\{\lambda_2^2 + C_2/(1-q')\}} = 38.3 \mu$. The relative displacements are larger here owing to the larger values of q' than in the former case.

If we used the value of a obtained from these formulæ we could calculate

* Rubens and Hollnagel, 'Sitzungsber.,' Berlin, 1910.

σ equal to $1/(1+a)$; this would give for rock salt $\sigma = 0.15$, and for fluorite $\sigma = 0.49$. But the preceding argument indicates that the calculations need considerable revision.

12. *Pressure and Temperature Displacement of Absorption Maxima.*

We shall consider now the displacement of absorption maxima under varying physical conditions, illustrating this by calculations for three cases in which suitable data are available.

Air.—The first example shows the effect of change of pressure and density in a gas, and we use Magri's experiments on air already examined in § 10. For a dispersion formula under ordinary standard conditions we have one obtained by C. and M. Cuthbertson* in the form

$$n-1 = \frac{4.6463 \times 10^{27}}{16125 \times 10^{27} - p^2}, \quad (34)$$

where p is frequency. Using the density of air as $\rho_0 = 0.00129$ we put this into a form suitable for present calculations and obtain

$$\frac{n^2-1}{\rho_0} = q + \frac{C_1}{\lambda^2 - \lambda_1^2}, \quad (35)$$

with $q = 0.44674$; $C_1 = 0.002493$; $\lambda_1^2 = 0.0055814$; $\lambda_1 = 0.074708 \mu$. To make the calculations definite we assume, as in § 10, that σ is zero in the standard condition, so that the quantity on the right of (35) is invariant as regards physical conditions and depends only on the atomic or molecular constitution. In any other physical state the quantity on the left of (35) is altered so that we have then

$$\frac{1}{\sigma + 1/(n^2-1)} \frac{1}{\rho} = q + \frac{C_1}{\lambda^2 - \lambda_1^2}.$$

The argument of the previous section shows that the observed maximum of absorption in any condition should be near the wave-length λ' given by

$$\lambda' = \sqrt{\left\{ \lambda_1^2 + \frac{C_1}{1/\rho\sigma - q} \right\}}. \quad (36)$$

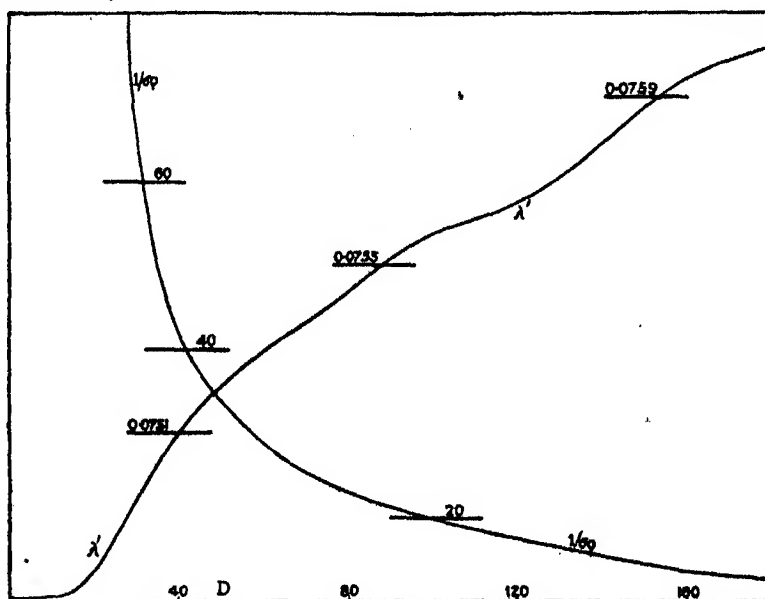
We obtain the following series of values of λ' corresponding to the values of the relative density D :—

* C. and M. Cuthbertson, 'Roy. Soc. Proc.,' 1909, A, vol. 83, p. 170.

Table XI.—Air.

D.	λ' .	D.	λ' .
1	0·07471—	69·24	0·07536
14·84	0·07471+	123·04	0·07566
28·58	0·07494	149·58	0·07586
42·18	0·07514	176·27	0·07601

The curves in the figure show the variation of λ' and of $1/\rho\sigma$ with the relative density D .



One may notice the slight initial increase of λ' , then a sharp rise between the values of 15 and 40 for D , followed by an approximately steady rise. We see also that $1/\rho\sigma$ decreases steadily with increasing density, falling sharply from an infinite value in the initial stages. No doubt the peculiarities at the lower values of D are due largely to the assumption that σ is zero initially. Still it does not seem possible to obliterate them entirely by assigning σ some small positive value initially; it is conceivable that there may be a stage at which the inter-molecular action specified by σ becomes suddenly appreciable. One may notice a possible analogy between the variation of λ' in the present case and the pressure displacement of lines in an emission spectrum.

Carbon Disulphide.—We can make calculations for CS_2 with the observations of Flatow and the values of refractive index obtained by Rubens for longer wave-lengths. If we know n for a given wave-length for a physical state of the medium defined by ρ and σ , the quantity $\{\sigma + 1/(n^2 - 1)\}\rho$ is independent of physical conditions; thus, by collecting observations at various temperatures, we can form an average set of values showing this molecular dispersion. With the convention adopted for assigning numerical values to σ , this would give, in fact, the values of $(n^2 - 1)/\rho$ for the substance as a gas at 0° and 760 mm. For reasons which have been indicated previously, it has not been thought advisable to try for a complete dispersion formula for this substance. However, four wave-lengths have been chosen, covering the range available, so as to form a four-constant formula to illustrate the present scheme. Using the values of σ given in §10 and the observations referred to above, we find

λ	0.274.	0.508.	1.037.	1.998.
Specific refraction	1.2368	0.8850	0.8274	0.8150

Before proceeding, we may notice the corresponding values of n for the vapour; using $\rho = 0.00342$, we obtain for these four wave-lengths in order the values 1.002113, 1.001512, 1.001414, 1.001393. The values of σ were, of course, calculated with the help of the observed value of 1.00148 for the wave-length 0.589. The values of n so calculated would be values for the vapour, on the assumption that the change from liquid to vapour involves only physical changes which can be expressed optically in terms of ρ and σ ; for instance, if some of the regions of absorption or resonance in the liquid were due entirely to molecular aggregates which were dissociated in the gaseous condition, then from this point of view the vapour would be optically a different substance. However, in most cases there does not appear to be an actual disappearance or creation of the principal dominating resonances, but only displacement and modification with changing conditions. We use the data above to determine the constants of a formula

$$\frac{1}{\sigma + 1/(n^2 - 1)} \frac{1}{\rho} = q + \frac{C_1}{\lambda^2 - \lambda_1^2} - k\lambda^2. \quad (37)$$

With sufficient approximation for our purpose, we find

$$q = 0.8123, \quad C_1 = 0.016077, \quad \lambda_1^2 = 0.03721, \quad k = 0.00036.$$

This gives a value of 0.1929 for λ_1 . If we take the dielectric constant to be given by $K = 2.6233 - 0.00249(t - 5^\circ)$ for liquid CS_2 , we obtain a mean value of 0.8420 for the left-hand side of (37) for λ infinite; using this, we may replace the term $-k\lambda^2$ by a single equivalent absorption region in the infra-red. We obtain in this way a term $C_2/(\lambda^2 - \lambda_2^2)$ with

now $q = 0.8420$, $C_2 = 2.4502$, and $\lambda_2 = 9.08 \mu$. Experiment has shown that carbon disulphide has specially strong absorption in the region between 6.6μ and 10μ .* In any given state the maxima of absorption occur at wave-lengths λ_1' and λ_2' , given, as in the previous sections, by expressions like $\{\lambda_1^2 + C_1/(1/\sigma\rho - q')\}^{\frac{1}{2}}$, when the dispersion formula has been put into a form suitable for the vicinity of the wave-length in question. Table XII shows the results for the gas and the liquid at three temperatures.

Table XII.—Carbon Disulphide.

	Liquid.			Gas.
	0°.	20°.	40°.	0°.
λ_1'	0.2159	0.2154	0.2149	0.1929
λ_2'	9.161	9.159	9.158	9.08

It is seen that λ' is displaced towards the shorter wave-lengths with increasing temperature. This appears to be the general rule for liquids, in contrast apparently to the behaviour of solids.

Water.—We examine now in the same manner Flatow's observations on water at five different temperatures; the values of σ were calculated in § 10, from a certain value of n for water vapour. Using these values we calculate the specific refraction for four wave-lengths; the following table shows the values at the various temperatures and the mean for each wave-length.

Table XIII.—Values of $1/\{\sigma + 1/(n^2 - 1)\} \rho$ for Water.

λ .	0°.	20°.	40°.	60°.	80°.	Mean.
274	0.67874	0.67868	0.67879	0.67409	0.67439	0.67894
361	0.64283	0.64225	0.64224	0.64229	0.64230	0.64228
480	0.62567	0.62571	0.62568	0.62566	0.62552	0.62565
589	0.61808	0.61815	0.61811	0.61803	0.61782	0.61804

Using the mean values and a density of 0.000809 for water vapour, with σ zero, we find the following values of n for these four wave-lengths in order: 1.000273, 1.000260, 1.000253, 1.000250; the last value is of course the one which was used in order to calculate the values of σ for the liquid.

* Cf. Winkelmann, 'Handbuch,' vol. 3, p. 350.

Using the mean values above, we calculate the constants of a dispersion formula of the type (37) and find

$$q = 0.60961; \quad C_1 = 0.003898; \quad \lambda_1^2 = 0.015110; \quad k = 0.00899.$$

The value of λ_1 is 0.1229μ ; we calculate now the values of λ_1' near which occur the maxima of selective absorption in the ultra-violet at the various temperatures. The following table shows the data and the results for the liquid, using $q' = 0.60947$.

t	0°.	20°.	40°.	60°.	80°.
σ	0.33622	0.33407	0.33439	0.33361	0.33364
ρ	0.999874	0.998235	0.99233	0.98331	0.97191
λ_1'	0.1294	0.1293	0.1293	0.1292	0.1291

In the formula for λ_1' it is the product $\sigma\rho$ which occurs as the variable; this decreases continuously in this case and we find a corresponding regular but very slight decrease in λ_1' with rising temperature. This result is in contradiction with that deduced by Flatow; he calculated the constants of a Sellmeier dispersion formula for each temperature and found a fairly regular increase in λ_1 with rising temperature, the values ranging from 0.126μ to 0.128μ approximately. There is, of course, no direct experimental evidence available in this case. In general the experimental data for the variation of absorption maxima with temperature are rather conflicting in character; the results appear to depend on circumstances such as the homogeneity of the medium and the character, selective or general, of the absorption. It has been stated that in several cases, at least in the ultra-violet, the maxima are displaced towards the shorter wave-lengths with increase of temperature for liquids, while for solids they move to the longer wave-lengths.

If we wish to study the resonance in the infra-red we must replace the term $-k\lambda^2$ of the dispersion formula by the effect of one or more equivalent terms; we try first a single term $C_2/(\lambda_2 - \lambda^2)$. If we take for the calculation the values of the dielectric constant given by Ratz, namely 87.7 at 0° and 79.9 at 20°, and if we use the corresponding values of σ given above, we obtain a mean value of 2.8787 for the specific refraction for infinite wave-length; hence C_2 and λ_2 are given by $C_2/\lambda_2^2 = 2.2691$; $C_2/\lambda_2^4 = 0.00899$. These give the values $C_2 = 572.7$ and $\lambda_2 = 15.88 \mu$. If, with the same notation as before, we form λ_2' in order to find the approximate position of the absorption maximum, we find that λ_2' ranges from about 79μ at 0° to 55μ at 80°. This large variation is due to the large values of C_2 and q' , and these come directly

from the abnormal value of the dielectric constant; the only inference is that if we insist on bringing the dielectric constant in this case under the same scheme as the ordinary dispersion, one resonance in the infra-red is not sufficient. It is well known that Sellmeier dispersion formulæ with the same assumption indicate $76\ \mu$ as the approximate position, and the subject has been studied experimentally recently. Using ice, Trowbridge and Spence* find no metallic reflection between $45\ \mu$ and $82.3\ \mu$; with water, Rubens and Hollnagel† obtain a similar result and also deduce that at $82.3\ \mu$ the refractive index is of the same order of magnitude as in the visible spectrum.

We may use this information in attempting to make up the term $-k\lambda^2$ from two resonance terms, $C_2/(\lambda^2 - \lambda_2^2) + C_3/(\lambda^2 - \lambda_3^2)$. To make the matter definite, we assume that n is 1.4 at $80\ \mu$; then, with this and the above data for the dispersion, we have the equations

$$\frac{C_2}{\lambda_2^2} + \frac{C_3}{\lambda_3^2} = 2.269, \quad \frac{C_2}{\lambda_2^4} + \frac{C_3}{\lambda_3^4} = 0.00899, \quad \frac{C_2}{80^2 - \lambda_2^2} + \frac{C_3}{80^2 - \lambda_3^2} = -2.13.$$

We have only three equations, with four unknown quantities; but to illustrate the calculations we assume a value for λ_2 , say $10\ \mu$. Then, solving the equations approximately, we find $C_2 = 89.2$; $C_3 = 24676$; $\lambda_3 = 134\ \mu$. Calculating now, as before, the positions of selective absorption corresponding to λ_2 at the various temperatures, we find they range from $14.2\ \mu$ at 0° to $12.5\ \mu$ at 80° . The principal absorption corresponding to λ_3 is far removed in the infra-red; the results appear to be fairly consistent with the absorption of water, and they confirm at least the necessity for more than one selective absorption in the infra-red.

13. Summary.

The chief results of the previous investigation may be summarised briefly in the following manner:—

1. The formal scheme of the theory is the representation of the effect of the physical state of the medium upon its dispersion by means of two variables: the density ρ , and a quantity σ expressing an effect of surrounding molecules.

2. A relation independent of σ is deduced, and is used as a test of the theory, namely, the difference of $\rho/(n^2 - 1)$ for any two physical states is independent of the wave-length.

3. As the result of an analysis of available experimental data, it appears that the scheme is sufficiently adequate for gases, for liquids, and for changes of state from gas to liquid. For solid substances, the two variables ρ and σ

* A. Trowbridge and B. J. Spence, 'Phys. Rev.', July, 1910.

† Rubens and Hollnagel, *loc. cit.*

are not sufficient to express all the facts, but it seems that the term involving σ must at least be taken into account in a complete theory.

4. It is shown that it is possible to include, either wholly or in part, the dispersion of artificial or natural double refraction in simple cases.

5. By assigning a standard state for the medium, gas at 0° and 760 mm., for which σ is zero, numerical values of σ are obtained for various substances in different states. Anomalies in molecular refractivity are ascribed, in part, to the variations in σ .

6. Using a type of dispersion formula involving ρ and σ , it is shown that the positions of the absorption maxima depend upon these quantities as well as upon the frequencies of the natural vibrations of the molecule. The consequent displacement of the maxima for varying conditions of pressure, temperature, and density are illustrated by analysing certain experimental data.

The Spectrum of Halley's Comet.

By CHARLES P. BUTLER, A.R.C.Sc., F.R.P.S., F.R.A.S.

(Communicated by Sir Norman Lockyer, K.C.B., F.R.S. Received November 5,—
Read November 24, 1910.)

[PLATE 7.]

Owing to the interference of high buildings it was impossible to arrange for observations of the comet spectrum during May from the Solar Physics Observatory at South Kensington. Sir Norman Lockyer therefore obtained permission to occupy the site on Fosterdown Fort, Caterham, which has already been selected as the future position of the Observatory.

No observations of value were possible during the first three weeks of May on account of exceptionally bad weather; but on May 23 and 26 photographs and visual observations of the spectrum were secured.

The spectrum was seen as a small nebulous cloud about 3' to 5' in diameter; with a binocular the central brightening due to the intense stellar nucleus became clearly visible. As a whole the comet was about as conspicuous as a second magnitude star, so that it was much fainter than had been expected. The curvature of the head was not so sharp as that seen in Comet 1910 α , giving the appearance of an elongated arc perpendicular to the tail extension when seen with moderate power.

Photographs of the comet were obtained with a Dallmeyer camera of

6 inches aperture and 5 feet focal length. The spectra were obtained with an ultra-violet spectrograph having a quartz lens of 2 inches aperture and 18 inches focal length, with an Iceland-spar prism of about 30° angle adjusted to avoid double refraction.

Although it was not possible to give sufficient exposure to record the tail extensions, the photographs of the nucleus and coma present several interesting features which assume importance when considered in relation to similar observations recorded elsewhere. The chief of these is the intermittent occurrence of a secondary condensation some distance from the principal nucleus. A photograph exposed on May 23 from 9.20 to 9.50 P.M. shows no appreciable trace of duplicity in the nuclear matter, while on a photograph exposed on May 26 from 9.40 to 10.10 P.M. there is a very distinct secondary condensation well separated from the principal nucleus, in position angle 270° and about $65''$ distant (Plate 7, figs. 1 and 2). Similar appearances are described in the reports from other observers.*

The colour of the head was pale lilac, being very similar to that of a vacuum-tube discharge in carbon compounds under feeble excitation without capacity. The tail was double and practically straight as far as it could be followed. On May 26 it was traced for about 8° to 10° from the head towards the south-east.

The spectrum was observed visually on May 22, 23, and 26 with a direct-vision spectroscope. No appreciable differences in the relative intensities or positions of the bands were perceptible for this interval of three days.

The nucleus showed a very strong continuous spectrum intensified by three bands in the yellow-green, green, and greenish-blue regions, presumably the usual cometary bands at $\lambda\lambda$ 5635 (int. 7), 5165 (int. 10), and 4737 (int. 7). Other intensifications of the continuous spectrum of the nucleus were suspected, but their positions could not be estimated with sufficient accuracy for record (fig. 3).

The spectrum of the coma surrounding the nucleus was seen to consist of these same three bands, extending the whole length of the slit. Careful examination failed to detect any continuous radiation in the coma spectrum. The spectrum of the tail could not be observed under the working conditions.

It is to be noted that the general appearance of the spectrum was somewhat different from that seen in the ordinary fluted spectrum of carbon compounds. The maximum intensity appeared to be more nearly at the

* 'Astronomische Nachrichten,' vol. 185, No. 4420, June 17, 1910; 'Comptes Rendus,' vol. 150, pp. 1496, 1659, June, 1910.

centre of each band, being somewhat similar to that seen in spectra under medium pressures rather than to the more complicated fluted structure under low pressure with electrical excitation. This appears to be borne out by the photographic spectra, where the maxima seem to be practically images of the nucleus and surrounding nebulosity of the coma. This appearance, however, may also be explained as being the integration of the brightest terminal components of the usual flutings by the objective prism spectrograph.

The weather conditions being so unfavourable it was only possible to obtain a photographic record of the brightest features of the spectrum of the nucleus. The three chief bands recorded visually are of course rendered of quite different relative intensities on the photographs, the least sensitive region of even the best isochromatic plates being the green.

The photographic spectrum shows two very conspicuous bright bands, about wave-lengths 4737 (int. 10) and 3884 (int. 6), with several other fainter bands at $\lambda\lambda$ 4050, 4360, 5165, and 5635. Their relative intensities will be best understood from the accompanying reproduction of the spectrum obtained on May 26 (fig. 4).

In enlarging the comet spectrum in one direction only, to provide a spectrum of sufficient width for reproduction, it is practically impossible to avoid introducing artificial lines due to the grain and minor imperfections of the plate. The bands noted as cometary bands, however, have all been found from the original negative, and are equally well shown on several enlargements. A small strip of the spectrum without vertical enlargement is given below for comparison (fig. 4).

In view of the fact that other photographs of the comet spectrum obtained elsewhere at a different time show important differences of intensity to those photographed at Fosterdown, it is of interest to inquire whether such differences are physical and indicative of real changes in the cometary radiation, or whether they may be due to atmospheric absorption (as has already been suggested by Deslandres) or optical differences between the instruments and photographic plates employed.

One of the chief differences noted is the relative inversion of intensity in the lines near $\lambda\lambda$ 4737 and 3884, as shown on photographs obtained in India on May 1, 3, 13, and at Fosterdown on May 26. The photographs at Fosterdown being taken with an instrument having a quartz-calcite optical train, consisting of a 2-inch quartz lens and Iceland-spar prism, specially adapted for recording radiations of short wave-length, these differences cannot be ascribed to instrumental absorption in the ultra-violet region.

Owing to the close proximity of the comet to the earth during the period

about the time of transit, the aspect of the head and nucleus of the comet was rapidly changing from day to day. Before the transit the part of the head facing the sun was principally visible; near the transit another part of the comet's head was visible from the earth; while after transit the hotter side of the coma would again gradually come into view. It is quite conceivable that this presentation of such different portions of the comet might exhibit notable differences of spectrum.

From a series of preliminary experiments it has been found that very remarkable changes of intensity of these carbon bands may be brought about by simple variations of the conditions of volatilisation; so much so, that this would probably serve as the more satisfactory reason for differences between various photographs of the comet's spectrum, provided, of course, that any known instrumental or atmospheric differences are duly considered.

I am indebted to Mr. J. P. H. Wilkie, photographer to the Observatory, for help in the preparation of the illustrations to this report.

The Distribution of Electric Force in the Crookes Dark Space.

By F. W. ASTON, B.Sc., A.I.C., Trinity College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S.—Received November 22, 1910,—
Read January 12, 1911.)

Introductory.

The electric force in the Crookes dark space and the negative glow has been the subject of a considerable number of investigations. The first determination was made by Schuster,* whose results indicate the presence of a positive charge of electricity, whose density decreases in geometrical progression as the distance from the cathode increases in arithmetical progression. Graham† found a curious drop in potential near the cathode, but Wehnelt‡, repeating these experiments, was unable to find this drop of potential, and ascribes it to the fact that the exploring points were not in the direct line of the current. Skinner§ came to the conclusion that all the fall of potential occurs at the surface of the cathode. Recently, Westphal|| has made a careful series of observations with cathodes of different metals

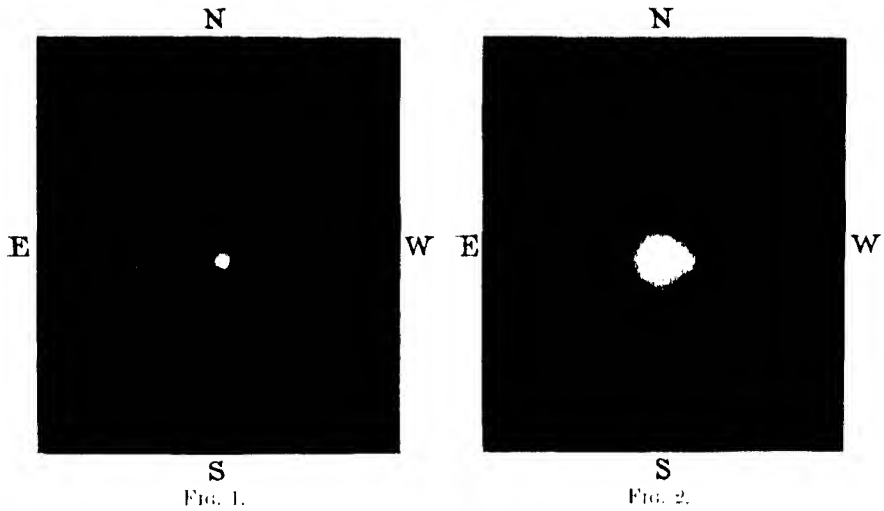
* 'Roy. Soc. Proc.' 1890, vol. 47, p. 526.

† 'Wied. Ann.', 1898, vol. 64, p. 49.

‡ 'Ann. d. Phys.', 1903, (4), vol. 10, p. 542.

§ 'Phil. Mag.', 1902, 6, vol. 2, p. 616.

|| 'Verhand. d. Deutsch. Phys. Ges.', 1910, vol. 12.



1910, May, 23 d. 9 h. 20 m. to 9 h. 50 m. 1910, May, 26 d. 9 h. 40 m. to 10 h. 10 m.
(Photographs of the Nucleus of Halley's Comet.)

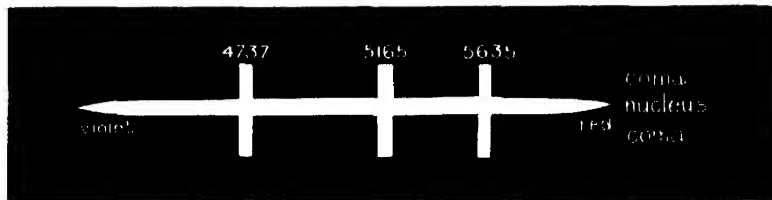


FIG. 3. Visual Observations of Spectrum, May 22, 23, 26.

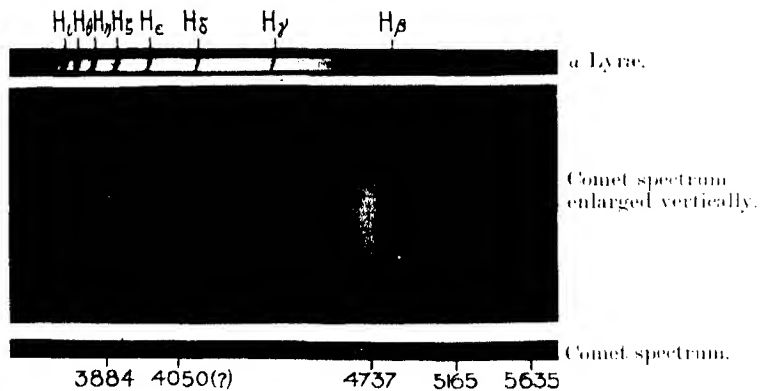


FIG. 4. Photograph of Comet Spectrum, with a Lyrae comparison.
(Quartz calcite Spectrograph, 2-inch aperture, 18 inch focus.)

in several gases, using a single exploring point, in which he finds a definite fall of potential—*e.g.* about 80 volts for Al in H_2 —at the surface of the cathode, the electric force a few millimetres away appearing from his curves nearly uniform.

Now all these measurements were made by introducing exploring sounds, *i.e.* metallic wires or points, into the discharge, the observers trusting to these taking up the potential of the gas by which they were surrounded. The danger of such assumption has been pointed out by Sir J. J. Thomson,* and for measurements made inside the dark space it seems entirely unwarranted.

Fortunately, however, there is an alternative method, which involves no doubtful assumptions, and does not introduce substantial obstacles into the discharge. Its simplicity and elegance cannot fail to appeal to anyone investigating this field of research. This method was suggested by Sir J. J. Thomson, and used by him recently in determining the potential distribution in the striated discharge;† it consists in shooting a beam of cathode rays transversely through the discharge, the deflection of these being taken as a measure of the electric force at that point.

It appeared to the author that this method might be used with advantage to determine the distribution of potential near the cathode under the conditions used by him in obtaining measurements of the length of the dark space,‡ these conditions being briefly:—

Electrodes in the form of circular discs filling the discharge tube, the latter being very much wider than the maximum length of the dark space, so that the edge effect will be comparatively small.

Current density always*greater than that necessary to cover the cathode with glow, and to cause the positive column to disappear.

It was to be expected, from the numbers obtained in the above research, that the electric forces to be measured would rise as high as 300 volts per centimetre. Now it can be easily shown that, for an electron to attain sufficient velocity to cross a tube 10 cm. wide under such a force with a small enough deflection, it is necessary for it to fall through a potential of about 20,000 volts. The principal problem to solve, therefore, was the design of a secondary discharge tube, which, while working at a pressure necessary to give a dark space of 2 to 3 cm. in the main tube, would deliver a homogeneous beam of cathode rays under a working potential corresponding to a centimetre spark in air.

* "Conduction of Electricity through Gases," 2nd ed., p. 531.

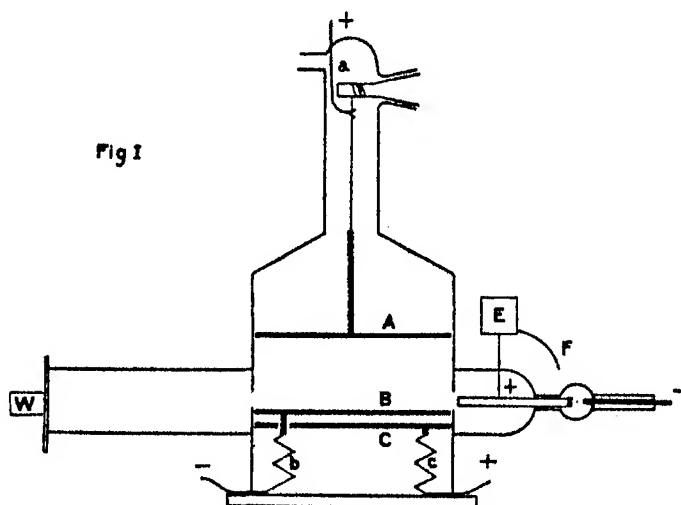
† 'Phil. Mag.,' Oct., 1909, vol. 18, pp. 441—451.

‡ F. W. Aston, 'Roy. Soc. Proc.,' 1907, A, vol. 79.

It was only after a tedious and dispiriting investigation, in which a large number of forms of secondary tube were tried—the whole apparatus having to be completely re-evacuated after each variation—that the necessary conditions were arrived at, when the rest of the research became comparatively easy.

Apparatus.

The arrangement of the apparatus is indicated in fig. 1. The main discharge tube is a large cylindrical bottle 12 cm. wide, with windows out in the sides, through which the exploring ray is to pass. A, B, and C are three aluminium discs, just filling the tube, and kept at fixed distances



apart by a framework of thin glass rods (not shown in the figure). A and B are 6.5 cm. apart, and form respectively the anode and cathode of the main discharge, which is maintained by a large battery of storage cells and controlled by a water resistance. B and C form a system of parallel plates 0.485 cm. apart, to which a known potential could be applied through the flexible leads *b* and *c*, to determine the deflection of the rays in a known uniform field.

As it is almost impossible to maintain a steady current with aluminium electrodes in the presence of mercury vapour, the old method of moving the electrodes up and down with a float supported on mercury was abandoned in favour of the device indicated in the figure. Into the neck of the bottle is fitted a vertical tube, to the side of which is attached a ground-glass joint (a good stop-cock does very well). The plug of this is elongated as a rod, over which is wound a flexible conducting cable made of a few strands of the

finest brass wire, and at the end of this is hung the apparatus to be moved, in this case the three discs. The method of fixing the point of support of the system, and also of supplying the anode lead, will be easily seen from the figure, the cable running under a slight tension through the copper wire fork α .

This simple arrangement proved quite faultless in practice, the plates being set at any required point with the greatest ease and accuracy.

At the one window of the main discharge tube was fixed a glass tube 28.5 cm. long, carrying a screen of powdered willemite w , at the other the secondary discharge tube. This in its final form is practically an X-ray bulb on a minute scale. The bulb is 1 cm. in diameter, the cathode is a piece of aluminium wire 1.5 mm. thick, the end is ground off perfectly flat and just emerges from the thick-walled tube into the bulb. The anode is a brass tube 10 cm. long, 5 mm. wide, plugged at both ends. The plug at the end nearest the cathode is of brass drilled with a 2 mm. hole, that at the other is of lead sheet pierced at the centre with the finest possible pinhole. The position of *both* electrodes must be adjusted with great nicety in order to get rays of sufficient hardness at the required pressure. The axis of the secondary discharge tube was set exactly parallel to the plane of the cathode. The secondary discharge was maintained by a small motor-driven Wimshurst, the anode being earthed. At first the discharge was intermittent, and the rays far from homogeneous, a difficulty appearing insuperable until it was accidentally found, by touching the bulb with the finger, that an earthed conductor F allowed to "brush" off on to the bulb rendered the discharge quite continuous if its distance was adjusted to suit the atmospheric conditions. When the apparatus was working well the image of the pinhole appeared on the screen over 40 cm. away as a sharp and almost perfectly steady circular spot, which could be read after a little practice to about 0.1 mm. The range of pressure over which suitable cathode rays were produced was exceedingly limited, and corresponded to a dark space in the main tube of about 3 cm., *whatever the nature of the gas*. By altering any of the dimensions of the secondary discharge tube another range could be obtained, but the above was used as being most satisfactory.

The pressure was not actually measured, but could be deduced from the length of the dark space; it ranged from about $\frac{1}{10}$ mm. in hydrogen to $\frac{1}{100}$ mm. in the other gases.

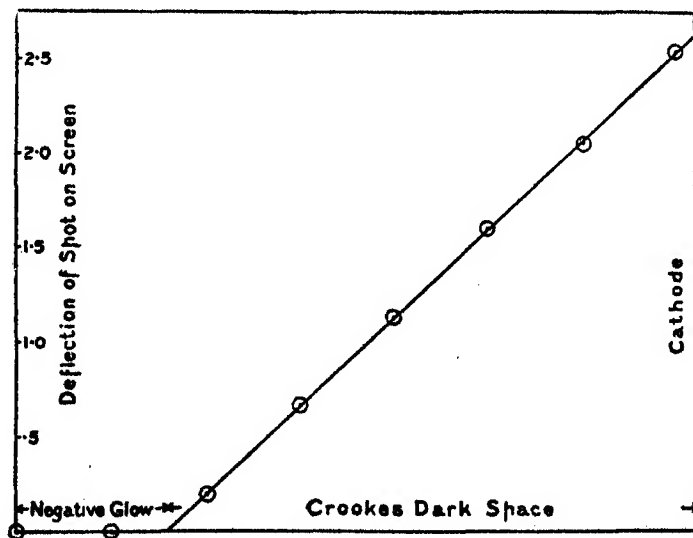
The potential between A and B was read on a Weston voltmeter, and by means of a double switch the same instrument was used for the determination of the standard field between B and C.

Experimental Procedure.

The apparatus was well washed with the gas to be used, and the pressure adjusted by an oil pump and a "charcoal liquid air" tube until the dark space was of suitable length and showed no tendency to alter, and the secondary discharge was also steady. The system of electrodes was then wound up until the pencil of cathode rays passed between B and C. When these two were both connected to earth a zero was obtained. A known potential was then put on between B and C, when a deflection of the spot was observed and measured on a scale attached to the screen. The plates were now lowered until the pencil passed through the dark space and the deflections taken corresponding to different distances from the cathode until the negative glow was reached. The plates were now raised and the observations checked on the return journey.

Results.

A typical set of readings obtained in this way is shown in the accompanying curve, in which deflections of the spot are plotted for different



positions in the dark space and negative glow. In the latter the deflection was always found to be zero, hence the electric force here is negligibly small compared with that in the dark space, a result agreeing with that found by the author in a previous paper (*loc. cit.*), "that the position of the anode, so long as it is in the glow, has no appreciable effect on the discharge." Measurable deflections commence *exactly* at the boundary of the dark space,

and within that region the deflection is proportional to the distance from the negative glow, the points lying practically on a straight line as indicated. (A critical examination of many sets of results shows a slight tendency for the curve to be a little steeper towards the ends than in the middle.)

This remarkably simple empirical result was obtained with hydrogen, air, oxygen, and argon, so that for these, and probably for all, gases under the conditions of these experiments *the electric force inside the dark space is in linear proportion to the distance from the edge of the negative glow.*

Since the total fall of potential across the dark space will be given by integrating the electric forces, it is clear that if we convert the deflections into electric forces this fall of potential will be the area of the curve bounded by the cathode and the edge of the negative glow, *i.e.* half electric force at surface of cathode multiplied by length of dark space. Before being able to obtain accurate measurements of this potential it will be necessary to find the correction for the curvature of the path of the exploring cathode beam.

Assuming the distribution found above, let μ = electric force at unit distance from the negative glow, then, if the length of the dark space is D , the equation of motion of an electron at distance y from the cathode is

$$\left(\frac{md^2y}{dt^2} = e\mu(D-y) \right).$$

If l is the diameter of the tube, and v the velocity of the particles in the cathode stream, entering at a point y' from the cathode and leaving at y , solving the above equation, we get

$$D-y = (D-y') \cos \frac{l}{v} \sqrt{\frac{\mu e}{m}},$$

whence
$$y-y' = (D-y') \left(1 - \cos \frac{l}{v} \sqrt{\frac{\mu e}{m}} \right).$$

This is the actual displacement in the tube; to obtain the total deflection at the screen at distance p from the tube, we must add p times the value of dy/dx at the point of emergence, which is

$$p \frac{dy}{dt} = \frac{p}{v} (D-y') \sqrt{\frac{\mu e}{m}} \sin \frac{l}{v} \sqrt{\frac{\mu e}{m}}.$$

Putting in the approximate values of sine and cosine, and adding, we obtain the total deflection

$$\frac{\mu(D-y')le(\frac{1}{2}l+p)}{mv^2} \left[1 - \frac{\mu e}{mv^2} \frac{l^2(\frac{1}{2}l+\frac{1}{2}p)}{\frac{1}{2}l+p} \right],$$

the part in square brackets being the correcting factor required.

Under a uniform field X , the total deflection is, in the same way,

$$\frac{Xe}{mv^2} l \left(\frac{1}{2} l + p \right).$$

Let K be the actual deflection when $y' = 0$, i.e. for a ray grazing the cathode, and E the uniform electric force necessary to give unit deflection, then, putting in the numerical values of p and l actually used in the experiment,

$$K = \frac{\mu D}{E} \left(1 - 0.053 \frac{\mu}{E} \right).$$

But the total fall of potential is

$$\begin{aligned} \frac{1}{2} \mu D^2 &= \frac{1}{2} \frac{KED}{(1 - 0.053 \mu/E)} \\ &= \frac{1}{2} \frac{KED}{(1 - 0.053 K/D)}, \text{ putting in approximate value of } \mu/E, \\ &= \frac{1}{2} E (KD + 0.053 K^2). \end{aligned}$$

The value of K is obtained by plotting the deflections as described above, and finding where the straight line drawn through them cuts the cathode.

Distance from cathode in cm.	Hydrogen.				Air.	Oxygen.			Argon.
0.1	10.6	16.8	22.0	25.8	25.0	19.9	21.5	28.7	26.5
0.6	8.8	13.3	18.2	20.5	20.4		17.5	22.8	21.0
1.1	7.1	10.5	14.4	16.0	15.5	12.5	13.9	17.5	17.0
1.6	5.6	8.0	11.0	11.5	11.0		10.8	12.0	12.5
2.1	4.0	5.4	7.8	6.6	7.2	6.0	7.0	6.9	8.2
2.6	2.5	3.2	3.6	1.9	2.6	3.0	3.5	0	4.0
3.1	0.2	0	0	0	0	0	0		0
3.6	0								
Length of dark space	3.20	3.10	3.10	2.81	2.86	3.05	3.10	2.70	3.02
Volts per cm. per cm. deflection	144	135	146	152	156	137	139	140	148
Total potential calculated in dark space	270	369	536	595	590	442	493	602	610
Potential between electrodes ...	265	375	530	610	583	445	495	610	620

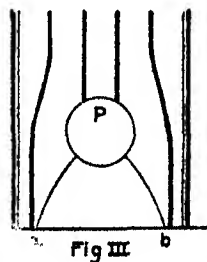
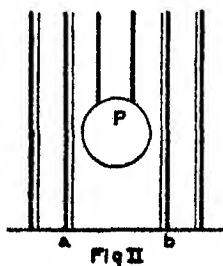
In the accompanying table are given the deflections observed, the fall of potential in the dark space calculated by the above formula, and the voltage actually observed between the electrodes. It will be seen that, although the voltage (and with it the current in the tube) was varied over a wide range,

the calculated fall of potential, though more often less than greater, never differs from the observed by more than experimental error. From this the author arrives at the conclusion that, under the conditions of the experiment, practically the whole of the potential fall takes place in the Crookes dark space, and is distributed within it in the form of a continuous parabolic field.

The so-called "Kathodensprung."

It will be seen that, considering the close agreement of the fall of potential in the dark space with that between the electrodes, it is difficult to find room for the fall of the order of 20 volts close to the surface of the anode observed by Skinner, and quite impossible to do so for one of 80 volts at the surface of the cathode recently measured with an exploring wire by Westphal (*loc. cit.*). One is therefore driven to the conclusion that the sound does not take up the correct potential when used near the cathode. A careful consideration of the conditions under which the experiments were performed suggests the following possible explanation.

There is little doubt that at the surface of the cathode, when steady discharge is taking place, streams of positive ions—"Canalstrahlen," represented in the figure by heavy lines—are falling upon the surface of the cathode, and by their impact liberating streams of negative ions—cathode rays, represented in the figure by light lines travelling in the opposite direction. Let P be a small material obstacle introduced into such a system, and let it for an instant be at the same potential as the cathode. Such an obstacle, if sufficiently small compared with the length of the dark space, will interfere inappreciably with the supply of + ions, the bulk of which are almost certainly generated near or in the negative glow, but it will absolutely prevent the bombardment of that part (*ab*, fig. 2) of the cathode immediately beneath it, which part will at once cease to liberate — ions.



P is now being bombarded with ions of only one sign, and its potential must inevitably rise. As this happens it will deflect the + ions passing

close to it out of their normal path, making the "shadow" or inactive part ab still larger (fig. 3), until finally its potential will rise so high that it is able to deflect to itself the $-$ ions generated at the boundaries of ab in sufficient numbers to exactly balance the supply of $+$ ions in whose direct path it still lies, when equilibrium potential will be established.

Since the equilibrium potential between the obstacle and the cathode is only concerned with the *relative* intensity of the supplies of $+$ and $-$ ions, it will be practically independent of the gas pressure and the current density, and, in fact, might be expected to behave very much as does Westphal's "Kathodensprung," which seems in all probability non-existent in a normal unobstructed discharge.

Theoretical Aspects of the Results.

A detailed enquiry into the theoretical considerations involved in the somewhat remarkable result of this investigation is beyond the scope of the present paper, but a few of the more salient points may be referred to with advantage.

Since the rate of change of electric force in the dark space is uniform, the latter must be a region in which the free electrification has a uniform excess positive density ρ , such that if V is the potential fall across the dark space and D its length, $\rho = V/D^2$.

The author has shown (*loc. cit.*) that if V is constant D varies very nearly universally as the pressure; hence for a constant voltage ρ varies directly as the square of the pressure. It, however, bears no simple relation to the voltage or the current density at constant pressure.

The assumption made for simplicity by the author in the above paper that the density of the free negative electrification in the dark space might be neglected is clearly incorrect, since the excess of positive ions must carry more current in the stronger parts of the field than they do in the weaker ones, so that in the latter ions of both signs must be present to maintain the flow. It appears, indeed, that the actual number of ions of both signs per cubic centimetre increases as we move away from the cathode, their algebraic sum being the constant ρ , which becomes zero with surprising suddenness at the edge of the negative glow.

If we suppose that at the surface of the cathode a constant fraction of the total current is carried by this excess of positive ions, and that their velocity is proportional to the field at that point, we obtain a value of the mobility $k_1 \propto cPD^3V^{-2}$, which is the same expression (with different constants) as that obtained on other premises in the above paper, and shown to be notably constant for a given gas.

The fall of potential across the new dark space discovered by the author in helium and hydrogen,* must, from the results of this investigation, be taken as $2Vd/D$ instead of $\frac{3}{4}Vd/D$, which works out at 20 volts for hydrogen, 40 volts for helium, but the considerations involved in the theory suggested for this phenomenon are not affected.

Summary of Results.

(1) The electric force in the negative glow is negligibly small compared with that in the dark space.

(2) The electric force in the dark space is very nearly in linear relation to the distance from the negative glow ; and, hence,

(3) The dark space is a region of uniform positive electrification ceasing with great suddenness in the negative glow.

(4) The total fall of potential inside the dark space, calculated from the results obtained, agrees within the error of experiment with that observed across the electrodes.

(5) The method of exploring points is inapplicable to the dark space, and the large falls of potential at the surface of the cathode, observed by its use, are probably non-existent in an unobstructed discharge.

In conclusion, the author wishes to express his indebtedness to Prof. Sir J. J. Thomson, both for the method employed and for his kind help and encouragement during the investigation.

* F. W. Aston, 'Roy. Soc. Proc.,' 1907, A, vol. 80.

*The Density of Niton ("Radium Emanation") and the
Disintegration Theory.*

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According to the disintegration theory of radioactive change, a definite number of atoms of radium break up per second, each evolving an α -particle which ultimately becomes a helium atom, leaving behind lighter molecules which form the gas known as "radium emanation," or niton. The identity of the α -particle after it has lost its electric charge with the helium atom has been convincingly proved by Rutherford and Geiger; and measurements of the volume of helium evolved from niton by Ramsay and Soddy, and from radium in equilibrium with its disintegration-products by Dewar, render it exceedingly probable that in each successive change from radium to radium D only one α -particle is expelled per atom.

If, then, the view is held that the radium atom on disintegration to niton splits up into two parts only, one of which is the α -particle, then the atomic weight of the resulting niton is $226.4 - 4 = 222.4$. On the other hand, it may be supposed that the disintegrating radium atom splits up into three or more parts; helium, and two other bodies of higher atomic weight, if three parts. On account of its greater mass, the heavier particle might be expelled below the critical velocity necessary for the formation of ions in the air, and might itself be non-radioactive; if this were the case, its presence in a solid state would almost certainly escape detection. There is no direct evidence against such a supposition, for the atomic weights of none of the products of the disintegration of radium have been determined. Experiment alone can settle this question of the true atomic weight of niton; but on account of the exceedingly small volume of this gas obtainable from a relatively large weight of radium, the experiment is by no means easy.

A number of investigators have sought to obtain the atomic or molecular weight by comparing the rates of diffusion of "emanation" and air or nitrogen.

Pierre Curie and Danne	found.....	176*
Bumstead and Wheeler	„	180†

* 'Comptes Rendus,' 1903, vol. 137, p. 1314.

† 'Amer. J. Sci.,' 1904, p. 37.

Rutherford and Miss Brooks found	176*
Makower „	100†
Chaumont „	70—100‡

Perkins compared the rate of diffusion with that of mercury vapour, also a monatomic gas, and found 235.§

Lastly, Debierne made use of Bunsen's method of causing the gas to issue through a minute perforation in a diaphragm of platinum, and as the result of a very concordant set of experiments, obtained the number 220 for the molecular weight.||

But none of these methods, however ingenious, can be accepted as conclusive, for the conditions are so different from those usually obtaining in ordinary work that no certain inference can be drawn.

In 1909¶ we attempted the solution of this problem in another way. We found it possible to determine the critical and boiling points of niton with less than one-tenth of a cubic millimetre of gas. Assuming it to belong to the inactive series of gases, we plotted the critical and boiling points of argon, krypton, and xenon against their atomic weights, and found these points to lie almost exactly on a slightly curved line. Extrapolation showed that for the emanation to lie either on the line connecting the boiling points or the critical points, it must possess an atomic weight approximating to 176. It was quite impossible to bring the value 222·4 anywhere near the extrapolated curves; but it must be observed that, as the curvature is slight, a small error in the constants of argon, krypton, or xenon might alter the curvature in the reverse direction, and so make more probable the higher atomic weight. We realised at the time that the results could not be accepted as certain, and that the only criterion must be the determination of the density of the gas. It is, however, remarkable that all the determinations quoted, with the exception of Makower's and Chaumont's, point to an atomic weight either of 176 or of 222; these are the tabular atomic weights of the immediate follower of xenon in the periodic table, on the one hand, and of the next member on the other. The members of the series are :—

Helium.	Neon.	Argon.	Krypton.	Xenon.	I.	II.
4	20	40	83	130	176	222

* 'Trans. R. S. Canada,' 1901.

† 'Phil. Mag.,' 1905.

‡ 'Le Radium,' 1909, vol. 6, p. 106.

§ 'Amer. J. Sci.,' 1908, p. 461.

|| 'Comptes Rendus,' 1910, vol. 150, p. 1740.

¶ 'Trans. Chem. Soc.,' vol. 93, p. 1073.

To determine the density of a gas, four separate measurements are essential—the volume, the temperature, the pressure, and the weight of the gas. In the present case, however, the problem was simpler, for the volume of niton at normal temperature and pressure accumulating in a given time from a known weight of radium is a constant and invariable quantity, and has been repeatedly measured. In 1908 Rutherford found this volume to be 0.61 cu. mm. per gramme of radium; Debierne in 1909 obtained the value 0.58 cu. mm., and these results were confirmed shortly afterwards by our own work,* which gave 0.601 cu. mm. Rutherford has been able to calculate this constant from the result of his beautiful experiment in which he actually counted the number of α -particles emitted from a known weight of radium, and the value found was 0.585 cu. mm. It may therefore be taken as certain that the error in this constant does not exceed 5 per cent. For our experiments this figure is unessential, since the actual volume of emanation from the total radium at our disposal had been measured.

The problem which we have attacked is the determination of the weight of emanation evolved in a given time from our total quantity of radium. The radium bromide solution from which the niton for these experiments was drawn was contained in three bulbs sealed on to a Töpler pump. The maximum measured quantity of emanation which can be extracted with the pump from the solutions in the bulbs is 0.127 cu. mm. By collecting the gas every eight days, the yield was only 76 per cent. of this quantity, so that the total volume obtainable for weighing scarcely exceeded 0.1 cu. mm. The weight of this volume, on the assumption that the atomic weight is 222, is less than 1/1400 mgrm. It is therefore evident that in order to weigh this minute quantity of gas with sufficient exactness, a balance turning with a load not greater than 1/100,000 mgrm. was a necessity. This seems an almost inconceivably small weight to attempt to measure, when one considers that the limit of sensibility of a delicate assay balance is about 1/200 mgrm., and that even the Nernst balance will hardly turn with a load smaller than 1/2000 mgrm.†

The successful construction of a balance capable of weighing these very minute quantities has been accomplished by Dr. B. D. Steele and Mr. Grant, of the University of Melbourne; thanks to their skill and ingenuity, they have constructed an instrument 100 times more sensitive than the Nernst micro-balance. Steele and Grant have published an account of their

* *Loc. cit.*, p. 1082.

† As we shall have to deal with very small weights, it is advisable to adopt a new unit; this is conveniently the millionth of a milligramme. The abbreviation here used for this is μ mgram.

balance,* and they have shown that a sensibility of $1/250,000$ mgrm. could be attained. After several trials we have been successful in constructing a similar instrument and in determining the density of the radium emanation with its help. It is only fair to state, however, that Dr. Brill, working in the laboratory of University College, improved the Nernst balance, so that it turned with $1/10,000$ mgrm. The subject was followed up later by Dr. Gwyer, also at University College, who introduced the hydrostatic method of determining small weights, the buoyancy of a small bulb containing a known weight of air being altered by the adjustment of the pressure in the balance case, constructed so that a vacuum could be made. We then corresponded with Dr. Steele, who was so obliging as to inform us of the principle and construction of his balance, then in an experimental stage.

The paper published by Steele and Grant renders a minute description of our balance unnecessary; but our balances (for several were constructed) differ in some small respects from theirs. The beam, for example, was made by placing thin silica rods in grooves carefully ruled on a smooth plane block of graphite, and then fusing the contiguous ends together in an oxygen coal-gas flame; in this way, a symmetrical beam, lying on a plane surface, was secured. If this condition is not fulfilled, the beam is apt to be deformed by small stresses set up in the quartz at the points of junction, as found by Steele and Grant. It is also necessary that the knife-edge shall be at right angles to the beam in two planes. This was managed by sealing the knife-edge on to the beam with a long guiding rod of silica attached to it, so that adjustment to a right angle is not difficult by trial and error; this guiding rod, when fused off, left a stem of a few millimetres in length, to which the platinised silica mirror was fused. By this device the mirror revolved without displacement when the balance was deflected. Another improvement was the direct sealing of a fine quartz fibre to the end of the beam, whereby a much freer suspension was attained. Again, while Steele and Grant weighed by displacement of the zero, our weighings were made by a null method, whereby the alteration of pressure brings the spot of light to its original position. In this way, any possible variation in the sensibility of the beam with its deflection from horizontality is avoided. To eliminate as far as possible temperature changes and also vibration, the balance is mounted on a stone pillar in a cellar, and the brass case stands inside a large box of bright tin-plate. The mirror is illuminated by a beam of light from a Nernst lamp, which reflects on to a millimetre scale about 3 metres away. The light is allowed to impinge on the mirror only when a reading is taken.

* 'Roy. Soc. Proc.,' A, 1909, vol. 82, p. 580.

The small counterpoise quartz bulb, which contains a known weight of air, serves instead of a set of weights. When the air pressure in the balance case is the same as that in the bulb the apparent weight of the air which it contains is nil. That is to say, the real weight of the air in the bulb is exactly counterpoised by the buoyancy of the air outside. In a vacuum the sealed-up air exerts its full weight, and at any intermediate pressure the arm of the beam carrying the bulb is loaded with a known fraction of this weight. The counterpoise bulb of the balance used by us has a capacity of 22.2 cu. mm., and the air which it contains weighs 0.027 mgrm., or 27,000 μ mgrm. (millionth milligrammes). A pressure change of 1/10 mm. can be easily read by a cathetometer, so that any object lighter than 27,000 μ mgrm. can be weighed with an accuracy of 3.55 μ mgrm.

By reading the pressure more exactly, say to 1/100 mm., the limit of accuracy could have been increased to one-tenth of the figure above, provided, of course, that the sensibility of the balance is great enough; to obtain this maximum degree of sensibility two important conditions have to be fulfilled. The centre of gravity of the beam must be most carefully adjusted, and the knife-edge must be perfectly straight and regular, even when viewed through a microscope with a half-inch objective. The final adjustment of the centre of gravity is made by volatilising away from the top of the centre rod, round which the beam is built, minute quantities of quartz in the oxy-coal gas blowpipe; this is a comparatively simple process. The making of the knife-edge gave a good deal of trouble, but in the end this difficulty was overcome. The edge itself is about 0.3 or 0.4 of a millimetre long, and is ground in the form of a right-angled prism on the end of a quartz rod, which is subsequently fused on to the beam. The grinding and polishing of the edge, which is a very delicate operation, was carried out for us by Messrs. Hilger and Co.

Our present balance is sensitive to about 2 μ mgrm.; its zero remains perfectly constant for days together. When the counterpoise bulb is removed, the zero of the balance is not altered by large changes of pressure within the case.

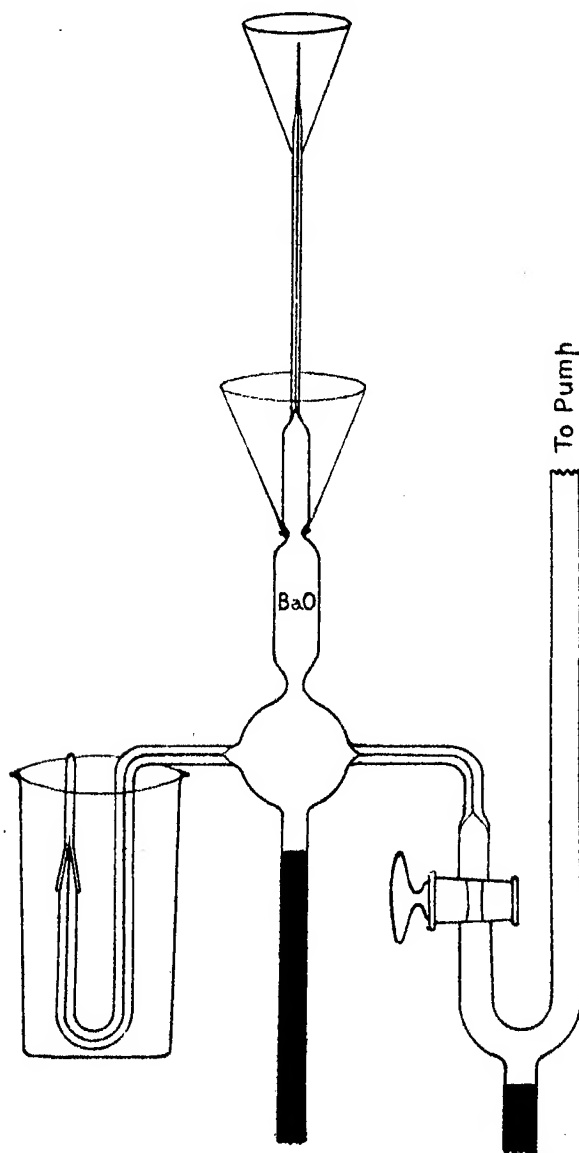
The standard of weight, which is, of course, the weight of the air in the counterpoise bulb, has been verified in the following way: A long measured length of very fine aluminium wire was weighed as accurately as possible on an assay balance. A small portion of this wire, about 2 mm. in length, was cut from the longer length in such a way that the cross-sections were as nearly as possible circular; it was then measured under a reading microscope, and its weight was determined in terms of the counterpoise-bulb on the micro-balance. The weight so determined agreed within 1 per cent.

with the weight calculated, on the assumptions that the wire was uniform, and that the weight of the small piece was directly proportional to its length.

For the measurement of the density of very small quantities of niton or of other gases, the following procedure was adopted:—The gas, of a volume of the order of 0.1 cu. mm., was forced by means of mercury into a fine capillary tube of about 1 mm. external and 0.2 mm. internal diameter, which was sealed on to the apparatus for purifying the gas (see figure). The upper end of this tube was drawn out into a finer very thin-walled tube, the extreme point of which was sealed. When necessary, the volume of the gas was measured at various pressures in the capillary tube, carefully calibrated for this purpose. After measurement, the tip of the tube was surrounded for some minutes with liquid air, in order to condense the gas; the volume of the gas was then considerably increased, so that any hydrogen still present should expand, and only a minute trace could remain at the top of the tube; the tube was then sealed at a distance of about 20 mm. below the tip, by aid of a pin-point gas flame. After most carefully cleaning and drying the small tube, it was lifted with platinum-tipped forceps, the tips of which had just been heated to redness, and placed in a little tightly-fitting "bucket," or external tube, of silica, suspended from one arm of the balance by quartz fibre; the pointed end of the density-tube was downwards, and the lower end of the bucket was slightly curved. A quartz counterweight, suspended to the same arm of the balance, was then adjusted, by fusing on or by volatilising off small pieces of silica, so that the beam was in balance at a pressure in the neighbourhood of 50 mm. After an hour or more the pressure in the case was exactly measured, and the position of the spot of light on the scale was noted. The bucket and tube were then removed with the platinum-tipped forceps; and, while it was held vertical inside a wider tube, the density tube was pressed down with a glass rod, cup-shaped at the end; the drawn-out point of the density-tube broke, but no splinters of glass could escape, for they were all retained in the bucket of silica. The bucket and its tube were then replaced on the balance and the air was exhausted; air was again admitted, and a second exhaustion was made; in this way the gas was removed from the interior of the density-tube, and replaced by air. The pressure was then adjusted to bring the zero point back again to its original position. With practice, the whole operation could be carried out in less than five minutes; this reduced the chance of error from the condensation of moisture on the glass and the settling of dust particles.

Before experimenting with the precious niton, the method was tested with

the less valuable xenon. Before freezing the gas its volume was measured; it amounted, at 0° and 760 mm., to 0.0977 cu. mm. It was then frozen, and the density-tube was sealed off and placed in its bucket on the



balance; after breaking the tip, the pressure change was 17.1 mm. (70—52.9); the temperature change was too small to affect the result; this pressure change corresponds to an apparent loss of weight of 608 μ mgm. But this number

does not represent the real weight of the xenon, for in the second weighing the tube is full of air, and therefore to the observed weight the weight of the air filling the tube at the temperature and pressure of the second weighing has to be added. The volume of the tube being known (for its length was measured), the weight of air under the conditions of weighing (52.9 mm. and 16°) proves to be 46 μ mgram.; hence the total weight is 654 μ mgram. A further correction has next to be applied to allow for the difference in buoyancy of the glass of the weighing-tube in the two weighings. This correction could, of course, be calculated, provided one knew the weight of the tube, the density of the quartz of the silica counterpoise on the end of the beam opposite to the objects to be weighed, and the density of the sample of glass forming the weighing-tube. It was found, however, to be more accurate and convenient to determine directly on the balance the magnitude of this correction for each experiment. For this purpose the counterpoise bulb containing air was replaced by a piece of quartz of almost exactly the same weight, and under the new conditions the variation of the zero point of the balance for a given change of pressure was determined. Knowing the weight corresponding to each scale-division displacement of the zero point, the variation in buoyancy of the open glass tube between the two weighings was easily and accurately calculated. In general, this correction is a somewhat large one, and amounts in this case to no less than one-seventh of the total weight of the gas. The reason for this is the large difference in weight between the density-tube and the contained gas. The density tube, as a rule, weighed about 30 mgrm., and the contained gas about 1/2000 mgrm.; hence the weight of the gas is to that of the vessel as 1 to 60,000, whereas, under ordinary conditions, when weighing 200 c.c. of gas, the ratio is about 1 to 600.

In this experiment, the correction for the buoyancy of the glass proved to be 91 μ mgram.; but there is still a correction to be applied, for there is a change of buoyancy due to the volume occupied by the gas itself. As the volume of the tube was known, this could be calculated with greater accuracy than it could be determined by experiment. In this case, the xenon occupied 0.536 cu. mm., and the difference in buoyancy of the air between the pressures 70 and 52.9 mm. (17.1 mm.) is

$$17.1 \times 0.536 \times 1.29/760 \times 1000 = 15 \mu\text{mgram.}$$

Had the sealed tube been weighed at the lower instead of the higher pressure (at 52.9 instead of 70 mm.), it would have weighed more; hence this correction is positive. The true weight of the xenon is therefore 654 - 91 + 15 = 578 μ mgram. The calculated weight of 0.0977 cu. mm. of xenon is 577 μ mgram. The exact agreement is doubtless a coincidence.

With niton, two sources of error made their appearance; in the first place, the density-tube became strongly electrified, and attracted dust particles and adsorbed air, and in the second, the tube was always at a higher temperature than the surrounding atmosphere during weighing,* and convection currents were liable to be set up in the air surrounding one limb of the balance. The first of these effects could not be entirely eliminated, but it was considerably reduced as regards dust by filtering the air through a long column of tightly packed cotton-wool before allowing it to enter the balance-case. In addition, the tube, after suspension from the beam of the balance, was, as a rule, gently heated by passing a non-luminous pin-pointed gas-flame quickly over its surface, thus burning off most of the attracted particles of dust. The same expedient was also adopted, before the second weighing, after the tube had been broken. Blank experiments showed that this procedure did not alter the weight of the tube in the slightest degree, provided it was perfectly clean; when dust-particles were present, however, there was always a small loss of weight.

The effect of convection currents was reduced as much as possible by weighing at a low pressure; in our five experiments, the final pressure varied from 87 to 13 mm.; and the concordance of the results precludes the possibility of any serious error from this source. It may also be noted that the density-tube, after removal of the niton, and during the second weighing, contained approximately the equilibrium amount of radium A, B, and C, the heating effect of which is a large fraction of the total heating effect of the emanation in equilibrium with its quick-change products; hence any error in the first weighing was partially compensated by a similar error in the second weighing. Finally, we would point out that convection currents, on account of the position and shape of the tube, have very little influence on the balance, and their presence should have been revealed by the oscillations of the beam and the position of the zero-point. No irregularity, however, was noticed, and we believe that this source of error produced only negligibly small effects.

Before proceeding to cite the experimental results, we have still to explain how the exact volume of niton weighed was ascertained. Taking as a basis our previous measurements, which proved the equilibrium amount of niton yielded by the total amount of radium at our disposal to be 0.127 cu. mm. at normal temperature and pressure, we had to determine what fraction of this amount was actually present in our weighing-tube. This was conveniently done by measurement of the γ -ray activity by help of a small aluminium electroscope. The procedure was as follows:—

* See Ramsay, 'Trans. Chem. Soc.,' 1907, vol. 91, p. 931.

The emanation was drawn off from the radium-bulbs at definite intervals of time, usually eight or nine days. After explosion of the mixed oxygen and hydrogen gases, it was allowed to stand for several hours, so that the quick-change products should accumulate, and its γ -ray activity was measured in the usual way. It was next introduced into the density-tube, and frozen there, as described for xenon, and the hydrogen was removed by pumping; about 10 per cent. of the niton was pumped off with the hydrogen, for the niton has some vapour-pressure at -195° . The γ -ray activity of the gas removed was compared with that in the sealed-off density-tube, after a suitable interval of time. Other measurements were made to determine the quantity remaining in the purifying apparatus; but in most cases this was negligible, and, as a rule, the radioactivity of the pumped-off gas, *plus* the radioactivity of the gas in the weighing-tube, were together equal, after corrections for the decay had been made, to the initial total radioactivity of the gas before it had been purified. It was found, however, that some niton had entered the walls of the weighing-tube; this fraction was estimated by determining the radioactivity of the empty tube, immediately after it had been weighed. Obviously, this emanation had not been removed by the pump. In the table which follows, this amount appears in the column "volume left in tube"; it has been subtracted from the total volume.

The operations of drawing and purifying the emanation, measuring its radioactivity, counterpoising and weighing the density-bulb, and measuring the radioactivity of the amount pumped off, as well as that in the weighing tube, required a long day, so that the density-tube could not be broken until 24 hours after the niton was drawn; the actual volume of niton present at the moment of fracture, however, was easily calculated from its known rate of decay.

As the quick-change products A, B, and C are short lived and change rapidly into D, and as D is a solid, it remains in the density-bulb and is not weighed, but the helium resulting from the change of niton into A, A into B, and C into D, escapes for the most part along with the niton; its weight must be calculated, and that of the escaping gas diminished by its amount, in order to arrive at the true weight of the niton.

Five experiments were made in order to determine the total loss of weight on opening the density-tube, and a sixth to obtain an estimate of the weight of the helium produced by the disintegration of the niton as far as radium D. For this purpose a density-tube was filled as described in the middle of the month of July, 1910; it remained counterpoised on the balance until October, when the conversion into D was practically complete. As the half-life period of D is about 14 years, it is unnecessary to consider

any further change. At the end of October the point of the density-tube was broken as usual, and the tube was again weighed, the loss in weight being due to the helium produced.

We must here chronicle the fact that during the three months in which the tube hung on the balance a continuous gain in weight was noticed, rapid at first, but attaining an end point; this amounted to 670 $\mu\text{mgrm.}$ On heating the tube, 1280 $\mu\text{mgrm.}$ were lost. The tube had not been heated before it was originally suspended on the balance; the gain was probably due to condensation of air on the electrified surface, and possibly, but improbably, to the deposition of dust. This gain of weight on standing is, however, not confined to electrified surfaces; a gold capsule, heated to redness before suspension, gained considerably in weight for two days. The density-tube was heated and re-suspended on the balance, and for three hours there was no alteration of weight. It was then broken and immediately placed on the balance, and weighed within five minutes, during which it might be expected that no change would occur; the loss of weight was 15 $\mu\text{mgrm.}$ The volume of the density-tube was 0.196 cu. mm.; the weight of air filling it at 37.7 mm. pressure and 18.5° C. was 12 $\mu\text{mgrm.}$; hence the total weight of helium was 27 $\mu\text{mgrm.}$; no correction for glass displacement of air was necessary, for the pressure did not vary during the readings.

The calculated weight of helium obtainable from 0.072 cu. mm. of niton, the amount present in the tube, on the assumption that each atom (or molecule) of niton loses three α -particles on disintegrating to RaD, should have been 38 $\mu\text{mgrm.}$; of this, only about three-quarters had been removed by the pump. It was necessary to seek for the remainder, which, we believed, had entered the glass of the weighing-tube.

Before removing it, however, we thought it worth while to attempt to dissolve the deposit of radium D from the walls of the weighing-tube, and to estimate its amount by loss. The closed end of the weighing-tube was cut off, and the rest of the tube placed in the bucket along with it, and weighed. The tube itself was then washed out with a mixture of two drops of nitric acid, previously purified by distillation from a silica bulb, and one of water; the solution was preserved. The tube was then washed with water and dried by aspirating through it a current of dry air; it was then replaced in the bucket and re-weighed. The loss was 831 $\mu\text{mgrm.}$ Supposing that the emanation, the calculated weight of which, assuming it to have the atomic weight 222.4, was 713 $\mu\text{mgrm.}$, had lost three α -particles, the weight should have been 674 $\mu\text{mgrm.}$ The difference, as we have proved by a subsequent experiment on the solubility of glass in dilute nitric acid, is due to the removal of sodium and calcium as nitrates. This must have

amounted in the case given to $831-674 = 157 \mu\text{mgrm.}$ We identified under the microscope crystals of sodium nitrate.

It is obvious that no importance can be attached to the latter half of this experiment, except in as much as it shows a loss of weight of the order required.

The weighing-tube still contained presumably occluded helium. It was placed in a silica tube, surrounded by a thicker-walled tube, also of silica, and it was connected with a Töpler pump and with an inverted siphon for introducing oxygen. The apparatus was freed from air and washed out several times with oxygen, so as to avoid introducing helium or neon from the air. About one-third of a cubic centimetre of oxygen was then admitted, and the silica tube was heated in a blow-pipe flame until the glass weighing-tube had completely fused; small bubbles were evolved. The oxygen, together with the gas evolved from the tube, was pumped off and introduced into an apparatus consisting of a calibrated capillary tube in communication with a minute bulb containing charcoal cooled with liquid air. After some hours the oxygen was completely absorbed by the charcoal, and the residual gas was measured. The correction for the unmeasured gas still remaining in the charcoal bulb was found to be 4 per cent. The volume was 0.042 cu. mm. at 0° and 760 mm. pressure, and its weight was therefore $8 \mu\text{mgrm.}$ The sum of the helium actually weighed ($27 \mu\text{mgrm.}$) plus that measured ($8 \mu\text{mgrm.}$) gives a total of $35 \mu\text{mgrm.}$, differing from the calculated amount ($38 \mu\text{mgrm.}$) by only $3 \mu\text{mgrm.}$ That the gas measured was pure helium was proved by surrounding the upper part of the capillary tube with tin-foil, and passing a discharge from a coil through it. The full spectrum of pure helium was seen, and no other lines.

This result has astonished us, as, perhaps, it may astonish our readers, but the conditions under which the last weighing was made were particularly favourable, since the tube was practically non-radioactive.

This experiment taught us that about one-quarter of the helium produced by the disintegration of the emanation and its products enters the walls of the weighing-tube, and is not removed by the pump; we have now all the data for calculating the density of niton. The results are given in the annexed table:—

Table of Results.

No. of experiment.	Time of accumulation.	Total volume of niton.	Volume pumped off.	Decay of niton.	Volume left in tube.	Volume weighed.	Apparent weight.	Weight of air replacing niton.	Correction for displacement due to glass and air.	Correction for weight of helium produced from niton.	True weight of niton.	Atomic weight of niton.
1	Day.	Cu. mm.	Cu. mm.	Cu. mm.	Cu. mm.	Cu. mm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	
1	8	0·0969	0·0052	0·0182	0·0007	0·0728	721	+ 31	-29 + 24	- 8	739	227
2	9	0·1017	0·0188	0·0163	0·0100	0·0566	477	+ 103	-16 + 15	- 7	572	226
3	9	0·1017	0·0135	0·0253	0·0039	0·0590	577	+ 37	-22 + 9	-10	591	225
4	8	0·0969	0·0119	0·0157	0·0016	0·0677	673	+ 10	-26 + 12	- 6	663	220
5	8	0·0969	0·0082	0·0152	0·0005	0·0730	704	+ 29	-33 + 16	- 6	710	218
Mean...												223

A complete reproduction of Experiment 5 may be given, to show how all the requisite data are obtained and utilised.

Volume of niton accumulated in 8 days = equilibrium quantity

× fraction surviving $0·127 \times 0·763 = 0·0969$ cu. mm.

γ-ray activity of this sample, divisions per hour 3996 divisions.

γ-ray activity of fraction pumped off..... 353 „

Hence amount pumped off $0·0082$ cu. mm.

Amount of niton in weighing-tube = $0·0969 - 0·0082 =$ $0·0887$ „

The weighing-tube was then counterpoised on the balance.

Pressure in balance-case 54·4 mm.

Zero on scale of beam of light reflected from mirror 155 „

Twenty-five hours after drawing, the weighing-tube was broken.

The gas pumped out, however, was not the original $0·0887$

cu. mm., but that volume multiplied by the decay-factor for

25 hours, $0·828$, viz. $0·07347$ cu. mm.

Pressure in balance-case after breaking the density-tube 34·7 mm.

Pressure-change = $54·4 - 34·7$ 19·7 „

Zero on scale after breaking 154 „

Difference of zero = $155 - 154 = 1$ mm. But from measurement,

10 mm. pressure = 77 scale divisions; hence 1 division

= $10/77 =$ $0·13$ „

This must be added to the pressure— $19·7 + 0·13 =$ $19·83$ „

The counterpoise-bulb contained $0·0270$ mgrm., or 27,000

μmgrm. of air. Its buoyancy was altered by $(19·83/760)$

× 27,000 = $703·8$ μmgrm.

But air entered the tube when it was broken; the volume of the density-tube, ascertained by previous calibration, was $0·522$ cu. mm.

Weight of this air at 34·7 mm. and $17^{\circ}\text{C.} = 0·522 \times 1290 \times 35/760$

× $273/290 =$ $29·2$ μmgrm.

The sum of these quantities, $703·8$ and $29·2$ 733 „

But the pressure was changed by 19·8 mm.; this alters the weight of the density-bulb by the weight of air corresponding to the difference in volume between the glass density-bulb and a silica one; as already described, this quantity was determined directly by replacing the air-bulb by a solid counterpoise of silica, and using the density-bulb as a measure of buoyancy. For 19·8 mm. the "glass-displacement" is equivalent to $-32\cdot8 \mu\text{mgrm.}$ A further correction has to be made, viz. the change of buoyancy due to the volume occupied by the gas itself. The volume of the density-tube was $0\cdot522 \text{ cu. mm.}$; the change of pressure was 19·8 mm.; hence the weight of this air for 19·8 mm. change $= 0\cdot522 \times 1290 \times 19\cdot8/760 \times 273/290 = 16 \mu\text{mgrm.}$ This is a positive correction; the weight, $733 \mu\text{mgrm.}$, must be diminished by the difference between $32\cdot8$ and 16 , say $17 \mu\text{mgrm.}$ The remainder is $716 \mu\text{mgrm.}$

The last correction to make is the subtraction of the weight of the helium produced by the decay of the emanation during its stay in the weighing-tube. Now

22,400 cu. mm. niton weigh, say, $222\cdot5 \text{ mgrm.}$, and
 0·0224 " " weighs " $222\cdot5 \mu\text{mgrm.}$

Each atom of niton gives three atoms of helium; hence, helium from $0\cdot0224 \text{ cu. mm.}$ niton weighs $12 \mu\text{mgrm.}$ The volume of emanation decayed in the weighing-tube is $0\cdot0887 \text{ cu. mm.} - 0\cdot0735 \text{ cu. mm.} = 0\cdot0152 \text{ cu. mm.}$, and the weight of three times that volume of helium is $8 \mu\text{mgrm.}$ One quarter of this has entered the glass and has not escaped, hence the helium removed weighed $6 \mu\text{mgrm.}$ That number deducted from 716 leaves $710 \mu\text{mgrm.}$ as the weight of the niton.

To return for a moment to its volume. The amount of niton in the weighing-tube was $0\cdot07347 \text{ cu. mm.}$ at the moment of pumping out. But some niton had penetrated its walls, and was not removed by the pump. That amount was estimated by comparing the γ -radioactivity of the weighing-tube after it had been weighed "empty" with that of the gas pumped off, which had, of course, diminished in radioactivity; this diminution corresponded with the time which elapsed since the last reading, and was measured to verify the constancy of the electroscope. The radioactivity of the residue left in the weighing-tube was, after correction for natural leak, 17 divisions per hour. The original radioactivity of the niton in the weighing-tube was $3996 - 353 = 3643$ divisions per hour; its volume in the weighing-tube when decay commenced was $0\cdot0887 \text{ cu. mm.}$; hence the "volume" left in the tube by the retention of niton in the walls was $(17 \times 0\cdot0887)/3643 = 0\cdot0005 \text{ cu. mm.}$ This, subtracted from $0\cdot07347 \text{ cu. mm.}$, the volume of niton in the tube at the moment of pumping out, leaves $0\cdot0730 \text{ cu. mm.}$ as the volume actually weighed.

All the data are now complete; $0\cdot0730 \text{ cu. mm.}$ of niton at 0° and 760 mm. pressure weighed $710 \mu\text{mgrm.}$ A litre weighs $9\cdot727 \text{ grm.}$; a litre of oxygen weighs $1\cdot429 \text{ grm.}$; and the molecular weight of niton is therefore **218**.

The nomenclature of Rutherford and Soddy, which has attained the provisional assent of the Brussels Congress, is advantageous as showing the relationship between the degradation-products of the various radioactive elements, but obscures any chemical relationship between the elements themselves. Were it consistently carried out, radium, which undoubtedly belongs to the group of alkaline-earth metals, would have to be named after uranium, a metal with no affinities with that group. The "emanation of radium" is a cumbrous name, and gives no indication of its position in the periodic table, a position which may now be taken as certain. To

show its relation to gases of the argon series, it should receive a similar name; and the spectrum, the freezing-point, the boiling-point, the critical point, the density of the liquid, and the density of the gas, the last establishing, without doubt, the atomic weight of the element, having been determined in this laboratory, it only remains to give it a name. The name "niton," Nt, which has been used in this paper, is suggested as sufficiently distinctive.

The research, of which the foregoing is an account, yields a further proof, if such were necessary, of the beautiful theory of the disintegration of the radioactive elements originally advanced by Rutherford and Soddy in 1902. The determination of the density of a gas, even with approximate exactness, has always been regarded as establishing its molecular weight, the accurate value of which may have been derived from other considerations. In the present case, these considerations are the result of the disintegration theory. Determinations by Madame Curie and by Thorpe of the atomic weight of radium show beyond all doubt that it differs little from 222.4. That four atoms of helium separate from one atom of radium is rendered almost certain from the work of Dewar, and from experiments by Rutherford, and by Ramsay and Soddy. That three atoms of helium are lost by niton on decay has been shown in the preceding pages. It follows that one helium atom must escape when radium changes into its emanation; hence the true atomic weight of the emanation must be 222.4. This number hardly differs from the mean of the atomic weight determinations given in this paper; and the disintegration theory receives a further confirmation.

On Atmospheric Oscillations.

By HORACE LAMB, F.R.S.

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Introduction.

1. The chief question discussed in this paper (§§ 6—12) is that of the free oscillations of an atmosphere whose temperature varies with the altitude; and in particular the case of a uniform vertical temperature-gradient is studied in some detail. For consistency it is assumed that the expansions and contractions follow the adiabatic law. The problem is treated as a two-dimensional one, the space co-ordinates involved being horizontal and vertical; and the more definite conclusions arrived at relate to the case where the (horizontal) wave-length is somewhat large in comparison with the height of the atmosphere.

The results are most easily interpreted when the temperature-gradient does not fall much below that characteristic of a state of convective equilibrium. The normal modes of oscillation then fall into well-defined types.

In the most important type, the motion of the air-particles is mainly horizontal, and independent of the altitude, and the waves may therefore be described as “longitudinal.” The velocity of propagation of progressive waves is found to be equal to \sqrt{gH} , where H denotes what may be called the “virtual height” of the atmosphere, *i.e.* the height of a “homogeneous atmosphere” corresponding to the temperature of the *lowest stratum*. That the result should come out intermediate in value between the velocity of sound in the lowest stratum, *viz.*, $\sqrt{\gamma gH}$, and the zero velocity corresponding to the zero temperature which is postulated in the higher regions was to be anticipated; but that it should be identical in form with that obtained on the hypothesis of an *isothermal* atmosphere whose expansions are subject to Boyle’s law,* the effect of the upward decrease of temperature being exactly compensated by the greater elasticity implied in the adiabatic law, is somewhat remarkable.

When the temperature-gradient falls distinctly below the “convective” value, the character of the oscillation is less simple. The wave-velocity is somewhat increased, but must always remain below the value $\sqrt{\gamma gH}$, which is the velocity of sound in the lowest stratum.

2. A second type of oscillations depends on the degree of stability of the atmosphere.

* Rayleigh, ‘Phil. Mag.’ (4), 1890, vol. 29, p. 173; ‘Scientific Papers,’ vol. 3, p. 335.

The work required to bring unit mass of air from the density ρ_1 to the density ρ_2 under the adiabatic condition $p/\rho^\gamma = p_1/\rho_1^\gamma$ is

$$\int_{\rho_1}^{\rho_2} p d\left(\frac{1}{\rho}\right) = \frac{p_1}{(\gamma-1)\rho_1} \left\{ \left(\frac{\rho_2}{\rho_1}\right)^{\gamma-1} - 1 \right\}. \quad (1)$$

Hence if we imagine two thin strata of equal mass, whose densities are ρ_1, ρ_2 , and pressures p_1, p_2 , to be interchanged, the work required to effect this will be, per unit mass,

$$\frac{p_1}{(\gamma-1)\rho_1} \left\{ \left(\frac{\rho_2}{\rho_1}\right)^{\gamma-1} - 1 \right\} + \frac{p_2}{(\gamma-1)\rho_2} \left\{ \left(\frac{\rho_1}{\rho_2}\right)^{\gamma-1} - 1 \right\} = \frac{\rho_2^{\gamma-1} - \rho_1^{\gamma-1}}{\gamma-1} \left(\frac{p_1}{\rho_1^\gamma} - \frac{p_2}{\rho_2^\gamma} \right). \quad (2)$$

If we avail ourselves of the notion of "potential temperature,"* *i.e.* the temperature \mathfrak{S} which any particular portion of air would assume if brought adiabatically to some standard density D , we have

$$p/\rho^\gamma = R\mathfrak{S}/D^{\gamma-1}, \quad (3)$$

where R is the constant of the formula

$$p = R\rho\theta, \quad (4)$$

θ denoting the absolute temperature. Hence (2) becomes

$$\frac{R(\rho_2^{\gamma-1} - \rho_1^{\gamma-1})(\mathfrak{S}_1 - \mathfrak{S}_2)}{(\gamma-1)D^{\gamma-1}}. \quad (5)$$

Hence if $\rho_2 > \rho_1$, we must for stability have $\mathfrak{S}_1 > \mathfrak{S}_2$; *i.e.* the potential temperature must increase upwards. Now, if y denote depth below a standard level, we have, in equilibrium,

$$dp/dy = g\rho; \quad (6)$$

and combining this with (3) and (4), we find

$$\frac{1}{\mathfrak{S}} \frac{d\mathfrak{S}}{dy} = \frac{1}{\theta} \left\{ \gamma \frac{d\theta}{dy} - \frac{(\gamma-1)g}{R} \right\}. \quad (7)$$

In convective equilibrium, where p/ρ^γ , and consequently \mathfrak{S} , is the same at all altitudes, we have

$$\frac{d\theta}{dy} = \frac{(\gamma-1)g}{\gamma R}. \quad (8)$$

This equilibrium, though stable for some types of disturbance (§ 8), is in other respects neutral. For complete stability, $d\mathfrak{S}/dy$ must be negative, and therefore

$$\frac{d\theta}{dy} < \frac{(\gamma-1)g}{\gamma R}. \quad (9)$$

When this condition is fulfilled, we have a series of possible modes of

* v. Bezold, 'Berl. Sitzb.', 1888, vol. 46.

oscillation whose periods, depending as they do on the extent to which the temperature-gradient differs from the convective value (8), are comparatively long. Oscillations of this character, governed by local conditions, must undoubtedly occur in the atmosphere, and may conceivably account for some of the minor fluctuations of the barometer.

There remains a third type of oscillations which, when the wave-length is moderately great, approximate to the character of waves propagated vertically in the atmosphere. These have been discussed in a previous paper by the author.* From a meteorological standpoint they can hardly be of importance.

3. The theory of the "longitudinal" waves is of interest in relation to the large-scale oscillations of the earth's atmosphere as a whole. This subject was treated by Laplace,† and is of some importance in connection with the suggestion put forward by Lord Kelvin‡ as to the origin of the semi-diurnal variation of the barometer. Laplace's investigation was based on the hypotheses of a uniform equilibrium temperature and an isothermal law of expansion, and on the further *assumption* that the vertical motion of the air-particles may be neglected.§ Since the circumstances are then practically those of sound-waves propagated horizontally, his results naturally involve the "Newtonian" velocity of sound, \sqrt{gH} , where H is the height of the homogeneous atmosphere corresponding to the assumed uniform temperature θ_0 , viz., $H = R\theta_0/g$.

The hypotheses referred to were, of course, adopted only for mathematical convenience. As representations of actual conditions they are very imperfect; and there is, moreover, great uncertainty as to the most suitable value to be attributed to θ_0 . It appeared to the writer that a firmer ground for quantitative conclusions would be gained if it were possible to calculate the wave-velocity (for long waves), even in the two-dimensional problem, on somewhat more natural suppositions as to the constitution of the atmosphere and the law of expansion.

In the actual atmosphere the temperature, as a rule, diminishes upwards, although (as we have seen) it is necessary for stability that the gradient should nowhere exceed the convective value. The special hypothesis of a *uniform* gradient, which is here adopted as a basis of calculation, is itself an artificial one; but in spite of the fact that it implies an upper limit to the atmosphere, it may claim to give, on the whole, a better representation of the

* 'Lond. Math. Soc. Proc.' (2), 1908, vol. 7, p. 122.

† 'Mécanique Céleste,' Livre 4, Chap. 5. See also Rayleigh, *loc. cit.*

‡ 'Roy. Soc. Edin. Proc.,' 1882, vol. 11; 'Math. and Phys. Papers,' vol. 3, p. 341.

§ Some such assumption is necessary to make the problem determinate, in the absence of a prescribed condition to be fulfilled, or approximated to, in the upper regions of the atmosphere.

true conditions than the isothermal view, on which, indeed, the earth's atmosphere is merely a local concentration of a medium diffused through space.

As regards the law of expansion, since permanent inequalities of temperature are postulated in the equilibrium condition, it is proper to ignore the transfer of heat between adjacent portions of the air during the oscillations. In any case, theory shows that the effect of conduction on such long waves as we have here in view may safely be neglected.*

The main conclusion of Laplace was that the free and forced oscillations of an atmosphere covering a globe, whether this be at rest or in uniform rotation, are identical with those of a liquid ocean of uniform depth H ; but in view of the nature of his premises, and of the uncertainty as to the temperature to be adopted in estimating the value of H , considerable doubt has been felt as to how far this analogy can be relied upon for quantitative results. The present investigation tends, I think, to show that inferences of this kind will not be very far from the truth, provided the temperature adopted be the mean temperature of the lower strata of the earth's atmosphere, so far as this can be ascertained. The formal adaptation of the theory of longitudinal waves to the case of an atmosphere of relatively small depth covering a globe would follow the same course as in Laplace's investigation.

4. As regards the semi-diurnal variation of the barometer, the passage of Kelvin's paper already referred to runs as follows:—

"The cause of the semi-diurnal variation of barometric pressure cannot be the gravitational tide-generating influence of the sun, because, if it were, there would be a much larger lunar influence of the same kind, while in reality the lunar barometric tide is insensible or nearly so. It seems, therefore, certain that the semi-diurnal variation of the barometer is due to temperature. Now, the *diurnal* term, in the harmonic analysis of the variation of temperature, is undoubtedly much larger in all, or nearly all, places than the *semi-diurnal*. It is then very remarkable that the *semi-diurnal term of the barometric effect* of the variation of temperature should be greater, and so much greater as it is, than the diurnal. The explanation probably is to be found by considering the oscillations of the atmosphere, as a whole, in the light of the very formulæ which Laplace gave in his '*Mécanique Céleste*' for the ocean, and which he showed to be also applicable to the atmosphere. When thermal influence is substituted for gravitational, in the tide-generating force reckoned for, and when the modes of oscillation

* This follows from the equations (due substantially to Kirchhoff and Rayleigh) given in the author's '*Hydrodynamics*,' 3rd edit., § 343. Radiation has a different tendency in this respect.

corresponding respectively to the diurnal and semi-diurnal terms of the thermal influence are investigated, it will probably be found that the period of free oscillation of the former agrees much less nearly with 24 hours than does that of the latter with 12 hours; and that, therefore, with comparatively small magnitudes of the tide-generating force, the resulting tide is greater in the semi-diurnal term than in the diurnal."

The first question which here arises, viz., whether as a matter of fact the earth's atmosphere has a mode of oscillation of the requisite type, with a period of about 12 mean solar hours, can at the present time be examined more closely than was possible at the date (1882) of the above extract. The free oscillations of an ocean of water of uniform depth covering a globe of the size of the earth, rotating with the same angular velocity, have been very fully investigated by Hough* in the course of his classical work on tidal theory. He finds, in particular, that in the case of the most important free oscillation having the same general character as a semi-diurnal tide wave (i.e. its most salient spherical harmonic constituent is the sectorial harmonic of the second order), the depth h for which the period is exactly 12 sidereal hours is given by

$$gh/4\omega^2a^2 = 0.10049,$$

where a is the earth's radius, and ω its velocity of rotation. This is evaluated at 29,182 feet. It is to be remarked, however, that throughout the calculation the mutual attraction of the disturbed fluid has been taken into account, whereas in the aerial ocean this influence must be quite insensible. If the disturbance were accurately of the type of a spherical harmonic of the second order the requisite modification would consist merely in multiplying the previous result by the factor

$$\frac{g_2}{g} = 1 - \frac{2}{3} \times 0.18093 = 0.89144,$$

where the decimal fraction in the second member is the ratio of the density of the water to the mean density of the globe, as adopted in Hough's computation. This would make

$$gh/4\omega^2a^2 = 0.08958.$$

As the result of a more direct calculation, using Hough's algorithm, together with such of his numerical results as are applicable, I find

$$gh/4\omega^2a^2 = 0.08986,$$

the last figure being somewhat doubtful. If we put $g = 32.200$, $\omega = 2\pi/86164$, $a = 20,902,000$, this gives

$$h = 25,930 \text{ feet.}$$

* 'Phil. Trans.,' A, 1897, vol. 191, p. 139. See pp. 164, 179.

The substitution of a mean solar for a sidereal half-day as the period involves a further slight diminution, which can be estimated pretty closely from another of Hough's results. He finds that for $gh/4\omega^2a^2 = 0.1$, the speed (σ) of the free oscillation in question is given by $\sigma/\omega = 1.9968$. Comparing this with the former result, we infer that for a period of 12 mean solar hours ($\sigma/\omega = 1.9945$) we must have $gh/4\omega^2a^2 = 0.09965$, about. Assuming that when mutual attraction is ignored this figure is to be reduced in the same ratio as the former one, we have, finally,

$$gh/4\omega^2a^2 = 0.08911,$$

or, with the previous numerical data,

$$h = 25,710 \text{ feet.}$$

It must be remembered, of course, that these numerical results can claim no greater accuracy than the theory on which they rest, in which, in particular, the ellipticity of the earth, which is of the order $1/300$, is neglected.

On the other hand, the value of H for air at 0°C. is about 26,200 feet, with an increase of about 96 feet for every degree above this temperature. The mean temperature of the air near the earth's surface is usually estimated at 15°C. This would make $H = 27,640$ feet; but a somewhat lower value for the mean temperature of the lower strata, away from the immediate influence of the ground, would perhaps be more appropriate.

Without pressing too far conclusions based on the hypothesis of an atmosphere uniform over the earth, and approximately in convective equilibrium, we may, I think, at least assert the existence of a free oscillation of the earth's atmosphere, of "semi-diurnal" type, with a period not very different from, but probably somewhat less than, 12 mean solar hours.

At the same time, the reason for rejecting the explanation of the semi-diurnal barometric oscillation as due to a gravitational solar tide seems to call for a little further examination. The amplitude of this variation at places on the equator is given by Kelvin as 0.032 inch. The amplitude given by the "equilibrium" theory of the tides is about 0.00047 inch.* Some numerical results given by Hough in illustration of the kinetic theory of oceanic tides indicate that in order that this amplitude should be increased by dynamical action some seventy-fold, the free period must suffer from the imposed period of 12 solar hours by not more than 2 or 3 minutes. Since the difference between the lunar and solar semi-diurnal periods amounts to 26 minutes, it

* The numerical values given on p. 520 of the author's 'Hydrodynamics' relate to the lunar tide, and are, moreover, by an oversight, stated as "amplitudes," instead of as "ranges."

is quite conceivable that the solar influence might in this way be rendered much more effective than the lunar. The real difficulty, so far as this point is concerned, is the *a priori* improbability of so very close an agreement between the two periods. The most decisive evidence, however, appears to be furnished by the *phase* of the observed semi-diurnal equality, which is accelerated instead of retarded (as it would be by tidal friction) relatively to the sun's transit.*

5. The concluding part of the paper (§§ 13, 14) is an attempt to examine more closely than has hitherto been done the theory of waves on a surface of discontinuity in the atmosphere. That such waves may play a part in meteorological phenomena has been pointed out independently by Helmholtz† and Lord Kelvin,‡ but both writers have confined themselves to analogies drawn from the case of superposed homogeneous liquids. It is to be observed that even on this view the disturbance extends, upwards and downwards from the plane of discontinuity, through a space which is an appreciable fraction, of the wave-length; hence, apart altogether from the influence of compressibility, the conditions of the question will be modified when the wave-length is such that the ordinary variation of density within this space becomes sensible. It seemed worth while to investigate the matter; but it must be acknowledged that when there are no currents, the discontinuity being one of temperature and density only, the analogy proves to be adequate, under such conditions as are likely to occur in the atmosphere, for a considerable range of wave-lengths. For very long waves it would break down, the disturbance ceasing to be even approximately concentrated in the neighbourhood of the plane of discontinuity. The discontinuity then becomes, in fact, an unimportant incident in the general upward diminution of density.

When there is a discontinuity of *velocity*, the upper fluid being in steady horizontal motion relative to the lower, the question, when compressibility is taken into account, is more difficult, and I have not been able to arrive at any very simple results. There can be no doubt, however, that the aforesaid analogy is sufficient in this case also for wave-lengths less than a certain limit. In particular, the dynamical instability pointed out by Kelvin§ will remain.

* 'Brit. Ass. Rep.,' 1908, p. 606. The forced tides due to diurnal and semi-diurnal waves of temperature have been studied by Margules, 'Wien. Sitzb.,' 1890, vol. 99, p. 204.

† 'Berl. Sitzb.,' 1889; 'Wiss. Abh.,' vol. 3, p. 309.

‡ 'Brit. Assoc. Rep.,' 1876; 'Math. and Phys. Papers,' vol. 4, p. 457.

§ 'Math. and Phys. Papers,' vol. 4, p. 76.

Theory of Long Atmospheric Waves.

6. We consider an atmosphere arranged in horizontal layers of uniform density. The motions contemplated are restricted to two dimensions, x, y , of which x is horizontal and y vertical, the positive direction of y being downwards. The equilibrium values of the pressure, density, and temperature are denoted by p_0, ρ_0, θ_0 ; these are functions of y only, and are subject to the hydrostatic condition

$$dp_0/dy = g\rho_0, \quad (10)$$

as well as to the general relation

$$p_0 = R\rho_0\theta_0. \quad (11)$$

The equations of small motion are, in the usual notation,

$$\rho_0 \frac{\partial u}{\partial t} = -\frac{\partial p}{\partial x}, \quad \rho_0 \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial y} + g\rho. \quad (12)$$

$$\frac{D\rho}{Dt} + \rho_0 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) = 0, \quad (13)$$

$$\text{where} \quad D/Dt = \partial/\partial t + u\partial/\partial x + v\partial/\partial y. \quad (14)$$

The expansions being supposed subject to the adiabatic law, we have also

$$\frac{Dp}{Dt} = c^2 \frac{D\rho}{Dt}, \quad (15)$$

$$\text{where} \quad c^2 = \gamma p_0/\rho_0 = \gamma R\theta_0, \quad (16)$$

i.e. c is the velocity of sound corresponding to the equilibrium temperature at the point considered. It is accordingly in general a function of y . If we put

$$p = p_0 + \pi, \quad \rho = \rho_0 + \delta, \quad (17)$$

and continue to neglect small terms of the second order, we have

$$\rho_0 \frac{\partial u}{\partial t} = -\frac{\partial \pi}{\partial x}, \quad \rho_0 \frac{\partial v}{\partial t} = -\frac{\partial \pi}{\partial y} + g\delta. \quad (18)$$

$$\frac{\partial \delta}{\partial t} + v \frac{d\rho_0}{dy} = -\rho_0 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right). \quad (19)$$

Also, from (15), (13), and (10),

$$\frac{\partial \pi}{\partial t} + g\rho_0 v = \frac{Dp}{Dt} = -\gamma p_0 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right). \quad (20)$$

Hence, eliminating δ and π , we find*

$$\left. \begin{aligned} \frac{\partial^2 u}{\partial t^2} &= c^2 \frac{\partial}{\partial x} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + g \frac{\partial v}{\partial x}, \\ \frac{\partial^2 v}{\partial t^2} &= c^2 \frac{\partial}{\partial y} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + (\gamma - 1)g \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + g \frac{\partial v}{\partial y}. \end{aligned} \right\} \quad (21)$$

* It may be noticed, parenthetically, that in the case of an isothermal atmosphere where c is constant, these equations are satisfied by

$$u = e^{-(\gamma-1)gy/c^2} f(ct-x), \quad v = 0.$$

If we now write

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = \chi, \quad \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} = \zeta, \quad (22)$$

we deduce from (21), by differentiation,

$$\frac{\partial^2 \chi}{\partial t^2} = c^2 \nabla^2 \chi + \left(\frac{d.c^2}{dy} + \gamma g \right) \frac{\partial \chi}{\partial y} + g \frac{\partial \zeta}{\partial x}, \quad (23)$$

$$\frac{\partial^2 \zeta}{\partial t^2} = - \left\{ \frac{d.c^2}{dy} - (\gamma - 1)g \right\} \frac{\partial \chi}{\partial x}, \quad (24)$$

where

$$\nabla^2 = \partial^2 / \partial x^2 + \partial^2 / \partial y^2. \quad (25)$$

The latter equation shows that an irrotational motion is not possible unless

$$\frac{d.c^2}{dy} = (\gamma - 1)g, \quad \text{or} \quad \frac{d\theta_0}{dy} = \frac{(\gamma - 1)g}{\gamma R}, \quad (26)$$

which we have seen to be the case of convective equilibrium. We note also that

$$\frac{Dp}{Dt} = -\gamma p_0 \chi, \quad (27)$$

by (20).

Eliminating ζ between (23) and (24), we obtain

$$\frac{\partial^4 \chi}{\partial t^4} = c^2 \nabla^2 \frac{\partial^2 \chi}{\partial t^2} + \left(\frac{d.c^2}{dy} + \gamma g \right) \frac{\partial^2 \chi}{\partial y \partial t^2} - g \left\{ \frac{d.c^2}{dy} - (\gamma - 1)g \right\} \frac{\partial^2 \chi}{\partial x^2}. \quad (28)$$

If we assume that x and t occur only through a factor $e^{i(kx + \sigma t)}$, the equations (21) take the forms

$$\left. \begin{aligned} \sigma^2 u + igkv &= -ikc^2 \chi, \\ -igku + \sigma^2 v &= -c^2 \frac{\partial \chi}{\partial y} - \gamma g \chi. \end{aligned} \right\} \quad (29)$$

whence

$$\left. \begin{aligned} (\sigma^4 - g^2 k^2) u &= ik \left\{ gc^2 \frac{\partial \chi}{\partial y} + (\gamma g^2 - \sigma^2 c^2) \chi \right\}, \\ (\sigma^4 - g^2 k^2) v &= -\sigma^2 c^2 \frac{\partial \chi}{\partial y} - g(\gamma \sigma^2 - k^2 c^2) \chi. \end{aligned} \right\} \quad (30)$$

From these, or from (28), we have

$$c^2 \frac{\partial^2 \chi}{\partial y^2} + \left(\frac{d.c^2}{dy} + \gamma g \right) \frac{\partial \chi}{\partial y} + \left[\sigma^2 - k^2 c^2 - \left\{ \frac{d.c^2}{dy} - (\gamma - 1)g \right\} \frac{gk^2}{\sigma^2} \right] \chi = 0. \quad (31)$$

7. So far, the vertical distribution of temperature is arbitrary. In the case of temperature diminishing upwards with a *uniform* gradient, to which we now proceed, there is an upper limit to the atmosphere. If we take the origin of y at this level, we have

$$\theta_0 = \beta y, \quad (32)$$

where β is the gradient in question. It easily follows from (10) and (11) that

$$\rho_0 \propto y^n, \quad p_0 \propto y^{n+1}, \quad (33)$$

where

$$n = g/R\beta - 1. \quad (34)$$

Also

$$c^2 = \gamma R\beta y = \gamma g y / (n+1). \quad (35)$$

Hence

$$\left. \begin{aligned} (\sigma^4 - g^2 k^2) u &= \frac{i\gamma g^2 k}{n+1} \left[y \frac{\partial \chi}{\partial y} + (n+1) \chi - \frac{\sigma^2}{gk} k y \chi \right], \\ (\sigma^4 - g^2 k^2) v &= \frac{-\gamma g^2 k}{n+1} \left[\frac{\sigma^2}{gk} \left\{ y \frac{\partial \chi}{\partial y} + (n+1) \chi \right\} - k y \chi \right], \end{aligned} \right\} \quad (36)$$

$$\text{and} \quad y \frac{\partial^2 \chi}{\partial y^2} + (n+2) \frac{\partial \chi}{\partial y} + \left\{ \frac{n+1}{\gamma} \frac{\sigma^2}{gk} + \frac{n\gamma - n - 1}{\gamma} \frac{gk}{\sigma^2} - k y \right\} k \chi = 0. \quad (37)$$

The meaning of the factor $(n\gamma - n - 1)/\gamma$, which appears in one of these terms, is to be noticed; viz. we have

$$\frac{n\gamma - n - 1}{\gamma} = \frac{\beta_1}{\beta} - 1, \quad (38)$$

where β_1 is the temperature-gradient in a state of convective equilibrium, as given by (8).

To solve (37) we put

$$\chi = e^{ky} \phi, \quad (39)$$

and obtain

$$y \frac{\partial^2 \phi}{\partial y^2} + (n+2+2ky) \frac{\partial \phi}{\partial y} + 2\alpha k \phi = 0, \quad (40)$$

where

$$2\alpha = \frac{n+1}{\gamma} \frac{\sigma^2}{gk} + \left(\frac{\beta_1}{\beta} - 1 \right) \frac{gk}{\sigma^2} + n+2. \quad (41)$$

This is integrable by series, the solution which is finite for $y = 0$ being

$$\phi = 1 - \frac{\alpha}{1 \cdot n+2} (2ky) + \frac{\alpha \cdot \alpha + 1}{1 \cdot 2 \cdot n+2 \cdot n+3} (2ky)^2 - \dots; \quad (42)$$

or, in the notation of Dr. E. W. Barnes,*

$$\phi = {}_1F_1(\alpha; n+2; -2ky). \quad (43)$$

The remaining solution of (40) is of the form

$$\phi \int \frac{e^{-2ky} dy}{y^{n+2} \phi^2}, \quad (44)$$

where ϕ stands for the series in (42). This is not admissible in the present

* See, for example, 'Camb. Trans.,' vol. 20, p. 253, where references to other papers are given.

If we had assumed $\chi = e^{-ky} \phi$, in place of (39), we should have found

$$\phi = {}_1F_1(n+2-\alpha; n+2; 2ky).$$

The comparison verifies a well-known identity; see Barnes, *loc. cit.*

question, since it becomes infinite as y^{-n-1} for infinitesimal values of y , whereas the condition to be satisfied at the upper boundary is $Dp/Dt = 0$, or $y^{n+1}\chi = 0$; see equations (27), (33).

The formulæ (36) now become

$$\left. \begin{aligned} (\sigma^2 - g^2 k^2) u &= \frac{i\gamma g^2 k}{n+1} \left[y \frac{\partial \phi}{\partial y} + (n+1) \phi + \left(1 - \frac{\sigma^2}{gk}\right) ky \phi \right] e^{ky}, \\ (\sigma^2 - g^2 k^2) v &= -\frac{\gamma g^2 k}{n+1} \left[\frac{\sigma^2}{gk} \left\{ y \frac{\partial \phi}{\partial y} + (n+1) \phi \right\} - \left(1 - \frac{\sigma^2}{gk}\right) ky \phi \right] e^{ky}, \end{aligned} \right\} \quad (45)$$

the factor $e^{i(\sigma t + kz)}$ being omitted here, as elsewhere, for brevity.

The condition that $v = 0$ at the lower boundary, where $y = h$, say, taken in conjunction with (41), determines the values of α and σ , the wave-length ($2\pi/k$) being supposed given.*

8. In the case of oscillations about convective equilibrium we have

$$\beta = \beta_1, \quad n = 1/(\gamma - 1). \quad (46)$$

It follows from (24) that $\partial^2 \xi / dt^2 = 0$; hence either $\xi = 0$, i.e. the motion is irrotational, or the period is infinitely long.

The conditions to which the *steady* rotational motions thus indicated are subject follow most directly from (21). These equations are now equivalent to

$$\left. \begin{aligned} \frac{\partial}{\partial x} \left\{ c^2 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + gv \right\} &= 0, \\ \frac{\partial}{\partial y} \left\{ c^2 \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + gv \right\} &= 0, \end{aligned} \right\} \quad (47)$$

by (26). Hence

$$(\gamma - 1) y \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) + v = \text{const.} \quad (48)$$

The choice of two functions, u, v , to satisfy this equation, together with the two boundary conditions, can be made in an infinite variety of ways.

The remaining types of disturbance are periodic in character. The formulæ (42) and (45) apply, with

$$2\alpha = \frac{n\sigma^2}{gk} + n + 2, \quad (49)$$

in place of (41). Since (42) makes

$$y \frac{\partial \phi}{\partial y} + (n+1) \phi = (n+1) \left\{ 1 - \frac{\alpha}{1 \cdot n + 1} (2ky) + \frac{\alpha \cdot \alpha + 1}{1 \cdot 2 \cdot n + 1 \cdot n + 2} (2ky)^2 - \dots \right\}, \quad (50)$$

* The case of apparent failure, where $\sigma^2 = gk$, does not arise. This would require, by (36),

$$y \frac{\partial \chi}{\partial y} + (n+1 - ky) \chi = 0, \quad \text{or} \quad \chi = Cy^{-n-1} e^{ky},$$

which violates the condition at the upper boundary.

the condition that $v = 0$ for $y = h$ may be written

$$(n+1)\frac{\sigma^2}{gk} {}_1F_1(\alpha; n+1; -2kh) - \left(1 - \frac{\sigma^2}{gk}\right)kh {}_1F_1(\alpha; n+2; -2kh) = 0. \quad (51)$$

A complete discussion of the equations (49) and (51) is out of the question, but the limiting form to which the results tend as the wave-length increases is easily ascertained. In the first place, it appears that when kh is small we have

$$\frac{\sigma^2}{gk} = \frac{kh}{n+1}, \quad (52)$$

approximately, since this ensures, by (49), that αkh is also small. If H denote the virtual height of the atmosphere, as defined above (§ 1), we have

$$H = h^{-n} \int_0^h y^n dy = h/(n+1). \quad (53)$$

The limiting value of the wave-velocity V is accordingly given by

$$V^2 = \sigma^2/k^2 = gH. \quad (54)$$

The bearing of this result has been discussed in the introduction.

The formulæ (45), (50), and (39) now lead to

$$\left. \begin{aligned} u &\propto i(n+1 - kh^2y + \frac{1}{2}k^2y^2), \\ v &\propto k(y-h), \end{aligned} \right\} \quad (55)$$

the factor $e^{i(\sigma t + kx)}$ being understood. These values fulfil, as they ought, the irrotational condition

$$\frac{\partial u}{\partial y} = \frac{\partial v}{\partial x} = ikv. \quad (56)$$

Since the ratio of the amplitude of v to that of u is of the order kh , the motion is mainly horizontal, and the present type of waves may accordingly be characterised as "longitudinal."

The remaining solutions of (49) and (51), when kh is small, involve finite as distinguished from infinitely small values of αkh . As will be seen presently (§ 11), they approximate to the character of waves propagated vertically in the atmosphere.

9. In the general case, where n is not restricted to the precise value $1/(\gamma-1)$, the relation between α and σ is as in (41). When kh is small we have still a longitudinal wave for which σ^2/gk is of the order kh , subject to a certain condition. The equation (51) leads again to the result expressed by (52) or (54), and substituting in (41) we find that the implied assumption that αkh is also small will be justified provided $\beta_1/\beta-1$ be small, *i.e.* provided the temperature-gradient falls only a little short of the convective value β_1 .

The limiting form of (42), when no assumption is made as to the order of magnitude of akh , is

$$\phi = 1 - \frac{2aky}{1 \cdot n + 2} + \frac{(2aky)^2}{1 \cdot 2 \cdot n + 2 \cdot n + 3} - \dots, \quad (57)$$

or in Dr. Barnes' notation,

$$\phi = {}_0F_1(n+2; -2aky), \quad (58)$$

whilst (50) becomes

$$y \frac{\partial \phi}{\partial y} + (n+1)\phi = (n+1) {}_0F_1(n+1; -2aky). \quad (59)$$

It appears from (41), without making as yet any special assumption as to the smallness of $\beta_1/\beta - 1$, that when akh is finite, whilst kh is small, the ratio σ^2/gk will be very small or very great.

In the former case we have

$$\frac{\sigma^2}{gk} = \left(\frac{\beta_1}{\beta} - 1 \right) \cdot \frac{1}{2\alpha} \quad (60)$$

ultimately, and the condition (51) becomes

$$(n+1) \left(\frac{\beta_1}{\beta} - 1 \right) {}_0F_1(n+1; -2akh) - 2akh {}_0F_1(n+2; -2akh) = 0. \quad (61)$$

Since

$${}_0F_1(n+1; -z) = \Pi(n) z^{-\frac{1}{2}n} J_n(2z^{\frac{1}{2}}), \quad (62)$$

in the notation of Bessel's functions, this may be written

$$\frac{1}{2} \omega J_{n+1}(\omega) = \left(\frac{\beta_1}{\beta} - 1 \right) J_n(\omega), \quad (63)$$

provided

$$\omega^2 = 8akh. \quad (64)$$

If ω be a root of (63), the corresponding frequency of oscillation is given by

$$\frac{\sigma^2}{gk} = \left(\frac{\beta_1}{\beta} - 1 \right) \cdot \frac{4kh}{\omega^2}, \quad (65)$$

and the wave-velocity by

$$V^2 = \left(\frac{\beta_1}{\beta} - 1 \right) \cdot \frac{4(n+1)gH}{\omega^2}, \quad (66)$$

H being defined as before by (53). This result again is accurate as a limiting form for increasing wave-length.

10. The equation (63) might be discussed, when n or $2n$ is integral, with the help of the tables of Bessel's functions, but it may be sufficient to consider the case where the ratio $(\beta_1 - \beta)/\beta$ is small. It may be noticed that the formula embraces *all* the modes of the present class, the longitudinal waves already discussed corresponding to the case of ω infinitesimal. The roots of (63) which relate to the remaining modes are now given by

$$J_{n+1}(\omega) = 0, \quad (67)$$

approximately; and in particular the first of these slightly exceeds the first finite root of (67).

In convective equilibrium we have $n = 2.5$, if $\gamma = 1.40$. The first finite root of $J_{7/2}(\omega) = 0$ is $\omega_1 = 7$, very nearly. Hence for oscillations about a state of very nearly neutral equilibrium we have

$$V = \left(\frac{\beta_1}{\beta} - 1\right)^{\frac{1}{2}} \times 0.53 \sqrt{gH}.$$

In the case of $n = 3$, which makes $(\beta_1 - \beta)/\beta = \frac{1}{4}$, a first approximation, given by (67), is $\omega_1 = 7.586$, and a second is easily found to be $\omega_1 = 7.624$. This leads to

$$V = 0.198 \sqrt{gH},$$

which is about one-fifth the velocity of the longitudinal type of waves.

As to the character of these slow rotational* modes, we find from (24)

$$\zeta = -i \left(\frac{\beta_1}{\beta} - 1\right) \cdot \frac{\gamma}{n+1} \cdot \frac{gk}{\sigma^2} \cdot \chi, \quad (68)$$

$$\text{or, by (65),} \quad \zeta = -\frac{i\gamma}{n+1} \cdot \frac{\omega^2}{4kh} \cdot \chi. \quad (69)$$

Having regard to the kinematical meaning of the functions ζ, χ , as defined by (22), we see that the rotational quality in the relative motion of a fluid element predominates over the dilatational. We learn also from (45) that when $y = 0$ the amplitude of v is to that of u in the ratio σ^2/gk , which is small. Since v vanishes at the lower boundary, we infer that the vertical component of the velocity is in general relatively small. The distribution of horizontal velocity depends ultimately on the function

$$y \frac{\partial \phi}{\partial y} + (n+1) \phi,$$

which varies as

$$(\omega y^{\frac{1}{2}}/h^{\frac{1}{2}})^{-n} J_n(\omega y^{\frac{1}{2}}/h^{\frac{1}{2}}),$$

if ω be the relevant root of (63), or less accurately of (67). In the case of the first root, after the small one, this expression changes sign once, and once only, as y increases from 0 to h . For $n = 3$, the change of sign occurs for $\omega y^{\frac{1}{2}}/h^{\frac{1}{2}} = 6.379$, or $y/h = 0.70$.

The general character of the types of disturbance at present under consideration is most easily apprehended in the case of a "standing" oscillation. If on the preceding expressions we superpose others which

* The rotational character is, of course, present also in the longitudinal waves, unless $\beta = \beta_1$ exactly, though to relatively slight extent.

differ only in the sign of σ , and reject the imaginary parts, we find, on discarding all but the most important terms, that

$$\begin{aligned} u &\propto \left\{ y \frac{\partial \phi}{\partial y} + (n+1) \phi \right\} \sin kx \cos \sigma t, \\ v &\propto -ky \phi \cos kx \cos \sigma t. \end{aligned} \quad (70)$$

The differential equation of the lines of (oscillatory) motion, viz.

$$v dx - u dy = 0, \quad (71)$$

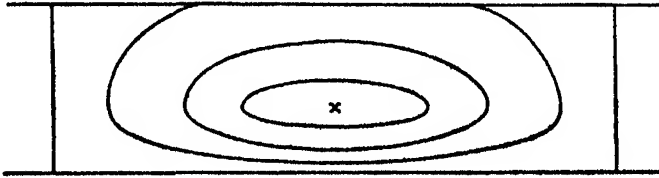
is accordingly satisfied by

$$y^{n+1} \phi \sin kx = \text{const.}, \quad (72)$$

or

$$y^{\frac{1}{2}(n+1)} J_{n+1}(\omega y^{\frac{1}{2}}/h^{\frac{1}{2}}) \sin kx = C. \quad (73)$$

If we put $C = 0$ we get the lines $y = 0$, $y = h$, $kx = s\pi$, but the former of these is only an approximation. The annexed figure indicates, without any attempt at minute accuracy, the general arrangement of the lines in the case of the lowest finite root of (67).



In the modes corresponding to the higher roots there are horizontal nodal planes ($v = 0$), in addition to the lower boundary.

Returning for a moment to the more important "longitudinal" type of motion first considered, we note that the formulæ (52), (54), cease to be accurate, even as limiting forms, when the ratio β_1/β differs appreciably from unity. The formulæ (65) and (66) will, however, still apply, ω being the lowest root of (63). As a numerical example, take the case where the temperature-gradient has only one-half the convective value, so that

$$(\beta_1 - \beta)/\beta = 1, \quad n = 6.$$

I find that the lowest root of

$$\frac{1}{2} \omega J_7(\omega) = J_8(\omega)$$

is $\omega = 4.96$, approximately, whence

$$V = 1.07 \sqrt{gH}.$$

The result must, of course, in any case be less than $\sqrt{(\gamma g H)}$, or $1.18 \sqrt{gH}$. The change of wave-velocity is accompanied by a change in the character of the oscillation, the variation of horizontal velocity with altitude now becoming sensible.

The preceding formulæ might also be used to estimate the rapidity of

falling away from the state of unstable equilibrium which prevails when $\beta > \beta_1$, the value of σ^2 given by (65) being then negative.

11. The modes for which σ^2/gk is large are easily accounted for. We have from (41)

$$\frac{\sigma^2}{gk} = \frac{2\gamma\alpha}{n+1}, \quad (74)$$

and from (45)
$$y \frac{\partial \phi}{\partial y} + (n+1)\phi = 0, \quad (75)$$

these being approximations which gain indefinitely in accuracy with increase of wave-length. On the present supposition that αkh is finite, notwithstanding the smallness of kh , (75) reduces to

$$J_n(\omega) = 0, \quad (76)$$

provided $\omega^2 = 8\alpha kh$, as in (64). If ω be a root of this equation, the corresponding frequency is given by

$$\sigma^2 = \frac{\gamma\omega^2}{4(n+1)} \cdot \frac{g}{h}. \quad (77)$$

These modes are in the limit identical with the waves of vertical displacement discussed in a paper already cited in § 2. The formulæ (45) show, in fact, that the ratio of the amplitude of u to that of v is for the most part of the order gk/σ^2 . If we put $h = \frac{1}{4}\gamma R\beta\tau_1^2 = \frac{1}{4}\gamma g\tau_1^2/(n+1)$, the equation (76) takes the form $J_n(\sigma\tau_1) = 0$, which is identical with equation (88) of the paper referred to.

12. It may be worth while, for the sake of the contrast, to give the theory of the oscillations of a heterogeneous but *incompressible* fluid, whose equilibrium density has a similar distribution.

We have now
$$\rho_0 \frac{\partial u}{\partial t} = \frac{\partial p}{\partial x}, \quad \rho_0 \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial y} + g\rho, \quad (78)$$

$$\frac{\partial \rho}{\partial t} + v \frac{d\rho_0}{dy} = 0, \quad (79)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \quad (80)$$

If we put
$$p = p_0 + \pi, \quad \rho = \rho_0 + \delta, \quad (81)$$

as before, we have

$$\rho_0 \frac{\partial u}{\partial t} = -\frac{\partial \pi}{\partial x}, \quad \rho_0 \frac{\partial v}{\partial t} = -\frac{\partial \pi}{\partial y} + g\delta. \quad (82)$$

$$\frac{\partial \delta}{\partial t} = -v \frac{d\rho_0}{dy}. \quad (83)$$

From (80) we have

$$u = -\frac{\partial \psi}{\partial y}, \quad v = \frac{\partial \psi}{\partial x}, \quad (84)$$

ψ being the stream-function. Substituting in (82), (83), and eliminating π and δ , we find*

$$\frac{\partial^2}{\partial t^2} \nabla^2 \psi + \frac{1}{\rho_0} \frac{d\rho_0}{dy} \left(\frac{\partial^3 \psi}{\partial y \partial t^2} + g \frac{\partial^2 \psi}{\partial x^2} \right) = 0. \quad (85)$$

If x and t occur only in the form $e^{i(\sigma t + kx)}$, we have

$$\frac{\partial^2 \psi}{\partial y^2} - k^2 \psi + \frac{1}{\rho_0} \frac{d\rho_0}{dy} \left(\frac{\partial \psi}{\partial y} + \frac{gk^2}{\sigma^2} \psi \right) = 0. \quad (86)$$

Also

$$v = ik\psi, \quad (87)$$

and

$$\frac{Dp}{Dt} = \frac{\partial \pi}{\partial t} + v \frac{d\pi}{dy} = i\sigma\pi + g\rho_0 v = \frac{i\sigma^2 \rho_0}{k} \left(\frac{\partial \psi}{\partial y} + \frac{gk^2}{\sigma^2} \psi \right). \quad (88)$$

If we now assume that

$$\rho_0 \propto y^n, \quad (89)$$

we have

$$y \frac{\partial^2 \psi}{\partial y^2} + n \frac{\partial \psi}{\partial y} + \left(\frac{ngk}{\sigma^2} - ky \right) k\psi = 0, \quad (90)$$

or writing

$$\psi = e^{ky} \phi, \quad (91)$$

$$y \frac{\partial^2 \phi}{\partial y^2} + (n + 2ky) \frac{\partial \phi}{\partial y} + n \left(1 + \frac{gk}{\sigma^2} \right) k\phi = 0. \quad (92)$$

The solution which is finite for $y = 0$ is

$$\phi = 1 - \frac{\alpha}{1 \cdot n} (2ky) + \frac{\alpha \cdot \alpha + 1}{1 \cdot 2 \cdot n \cdot n + 1} (2ky)^2 - \dots, \quad (93)$$

or

$$\phi = {}_1F_1(\alpha; n; -2ky), \quad (94)$$

if

$$2\alpha = n \left(1 + \frac{gk}{\sigma^2} \right). \quad (95)$$

The second solution becomes infinite as y^{-n+1} for $y = 0$, and is therefore excluded, in virtue of (88), by the condition that Dp/Dt must vanish at the upper boundary. Since, by (87), $\psi = 0$ for $y = h$, we have

$${}_1F_1(\alpha; n; -2kh) = 0. \quad (96)$$

This determines α , and the value of σ^2 follows from (95).

It is obvious that, when kh is small, (96) is not satisfied by finite values of α . If α be large, but so that αkh remains finite, the equation (96) tends to the form

$${}_0F_1(n; -2\alpha kh) = 0, \quad (97)$$

or

$$J_{n-1}(\omega) = 0, \quad (98)$$

provided

$$\omega^2 = 8\alpha kh. \quad (99)$$

If ω be a root of (98), we have

$$\frac{\sigma^2}{gk} = \frac{n}{2\alpha} = \frac{4n}{\omega^2} \cdot kh, \quad (100)$$

* Cf. Love, 'Lond. Math. Soc. Proc.' (1), 1891, vol. 22, p. 307.

and therefore, for the wave-velocity,

$$V^2 = \frac{\sigma^2}{k^2} = \frac{4n(n+1)}{\omega^2} \cdot gH. \quad (101)$$

Thus, if, for the sake of comparison with §7, we put $n = 2.5$, we have $\omega_1 = 4.491$, whence

$$V = 1.32 \sqrt{gH}. \quad (102)$$

That the frequency should be increased by the incompressibility was to be expected; that the effect is so considerable is due to the great modification which is caused in the character of the fundamental modes.

The modes corresponding to the higher roots of (98) have horizontal nodal planes, and the frequencies form, by (101), a *descending* series,* as in the case of (65).

Waves at a Surface of Discontinuity.

13. When we proceed to examine the case of waves propagated along a horizontal plane where the equilibrium temperature is discontinuous, it may be sufficient to suppose the temperature uniform throughout each of the regions, above and below this plane, to which the influence of the waves extends. The plane in question is taken as the plane $y = 0$, and the dependent variables relating to the upper region will be distinguished by accents.

The formulæ of §6 will therefore apply to the lower region, with the simplification that c is a constant; so that (31) becomes

$$c^2 \frac{\partial^2 \chi}{\partial y^2} + \gamma g \frac{\partial \chi}{\partial y} + \left\{ \sigma^2 - k^2 c^2 + \frac{(\gamma-1)g^2 k^2}{\sigma^2} \right\} \chi = 0. \quad (103)$$

This is satisfied by $\chi = C e^{\lambda y}$, (104)

provided $\lambda^2 + \frac{\gamma g}{c^2} \lambda + \left\{ \frac{\sigma^2}{c^2} - k^2 + \frac{(\gamma-1)g^2 k^2}{\sigma^2 c^2} \right\} = 0. \quad (105)$

We are seeking for a type of motion analogous to that of waves on the interface of two *liquids* of different densities, in which case the values of λ are $\pm k$. We assume, provisionally, that in our case also the roots of (105) are real and of opposite signs; moreover, since the disturbance is to vanish for $y = \infty$, the negative sign is to be taken.

For the upper region we shall have

$$\chi = C' e^{\lambda' y}, \quad (106)$$

with a similar determination of λ' ; but the *positive* root is now the appropriate one.

* Cf. Rayleigh, 'Lond. Math. Soc. Proc.' (1), 1883, vol. 14, p. 170; 'Scientific Papers,' vol. 2, p. 200.

If η denote the ordinate of the surface of separation, as affected by the waves, we have

$$\partial\eta/\partial t = v \quad (107)$$

for $y = 0$; and the pressure in either fluid at the point (x, η) is to be found by putting $y = 0$ in the corresponding value of the expression

$$p_0 + \pi + \frac{\partial p_0}{\partial y} \eta. \quad (108)$$

Differentiating with respect to t , we see that Dp/Dt must be continuous at the interface.* This involves, by (27), the continuity of χ , so that the constants C, C' in (104) and (106) must be equal. Again, it follows from (107) that v must be continuous, whence, by (30),

$$\sigma^2 c^2 \lambda - g k^2 c^2 + \gamma g \sigma^2 = \sigma'^2 c'^2 \lambda' - g k'^2 c'^2 + \gamma g \sigma'^2. \quad (109)$$

This, together with the two equations of the type (105), determines the values of λ, λ' , and σ .

To obtain a solution, we denote the two equal members in (109) by μ ; thus

$$\lambda = \frac{\mu}{\sigma^2 c^2} + \frac{g k^2}{\sigma^2} - \frac{\gamma g}{c^2}, \quad \lambda' = \frac{\mu}{\sigma'^2 c'^2} + \frac{g k'^2}{\sigma'^2} - \frac{\gamma g}{c'^2}. \quad (110)$$

Substituting in (105), we have

$$\mu^2 + g(2k^2 c^2 - \gamma \sigma^2) + (\sigma^4 - g^2 k^2)(\sigma^2 - k^2 c^2) c^2 = 0, \quad (111)$$

with a similar equation in which c is replaced by c' . Writing these two equations in the form

$$\mu^2 + P\mu + Q = 0, \quad \mu^2 + P'\mu + Q' = 0, \quad (112)$$

and eliminating μ , we have

$$(P - P')(PQ' - P'Q) + (Q - Q')^2 = 0. \quad (113)$$

Now

$$\left. \begin{aligned} P - P' &= 2gk^2(c^2 - c'^2), \\ Q - Q' &= (c^2 - c'^2)(\sigma^4 - g^2 k^2)\{\sigma^2 - k^2(c^2 + c'^2)\}, \\ PQ' - P'Q &= g(c^2 - c'^2)(\sigma^4 - g^2 k^2)\{\gamma\sigma^4 - \gamma\sigma^2 k^2(c^2 + c'^2) + 2k^4 c^2 c'^2\}. \end{aligned} \right\} \quad (114)$$

Hence

$$(\sigma^4 - g^2 k^2)\{\sigma^2 - k^2(c^2 + c'^2)\}^2 + 2g^2 k^2\{\gamma\sigma^4 - \gamma\sigma^2 k^2(c^2 + c'^2) + 2k^4 c^2 c'^2\} = 0. \quad (115)$$

This is of the fourth degree in σ^2 , but one root only is relevant to the present question. The common root of (112) is

$$\mu = \frac{PQ' - P'Q}{Q - Q'} = \gamma g \sigma^2 + \frac{2gk^4 c^2 c'^2}{\sigma^2 - k^2(c^2 + c'^2)}, \quad (116)$$

* This might almost have been assumed at once; but it is to be observed that it would not give the correct condition to be satisfied at the common boundary of two currents.

whence

$$\left. \begin{aligned} \frac{\lambda}{k} &= \frac{gk}{\sigma^2} \cdot \frac{\sigma^2 - k^2(c^2 - c'^2)}{\sigma^2 - k^2(c^2 + c'^2)}, \\ \frac{\lambda'}{k} &= \frac{gk}{\sigma^2} \cdot \frac{\sigma^2 - k^2(c'^2 - c^2)}{\sigma^2 - k^2(c^2 + c'^2)}. \end{aligned} \right\} \quad (117)$$

If we now write

$$a^2 = \frac{1}{2}(c^2 + c'^2), \quad b^2 = \frac{1}{2}(c'^2 - c^2), \quad (118)$$

$$x = \sigma^2/k^2 a^2, \quad \omega = g/ka^2, \quad (119)$$

the equation (115) becomes

$$x^2(x-2)^2 + \omega^2 \{(2\gamma-1)x^2 - 4(\gamma-1)x - 4b^4/a^4\} = 0; \quad (120)$$

$$\text{whilst} \quad \frac{\lambda}{k} = \frac{x+2b^2/a^2}{x(x-2)} \omega, \quad \frac{\lambda'}{k} = \frac{x-2b^2/a^2}{x(x-2)} \omega. \quad (121)$$

It is to be noticed that

$$\frac{b^2}{a^2} = \frac{c'^2 - c^2}{c'^2 + c^2} = \frac{\rho - \rho'}{\rho + \rho'}, \quad (122)$$

where ρ, ρ' , are the equilibrium densities at the plane $y = 0$, on the two sides.

For sufficiently small wave-lengths, ω and x are very small, and the root of (120) with which we are concerned is $x = \omega b^2/a^2$, approximately, whence

$$\sigma^2 = \frac{\rho - \rho'}{\rho + \rho'} gk, \quad \lambda = -k, \quad \lambda' = k, \quad (123)$$

as in the case of superposed incompressible fluids.*

To examine the matter further, the simplest procedure is to tabulate the function

$$x^2 = \frac{a^2(x-2)^2}{4b^4/a^4 + 4(\gamma-1)x - (2\gamma-1)x^2} \quad (124)$$

for a series of suitable values of x . The only case of real interest is where the discontinuity of temperature is very slight, so that b^2/a^2 is a small fraction. The following table gives a few results calculated on the supposition that $b^2/a^2 = \frac{1}{100}$, with $\gamma = 1.40$. The abrupt step in temperature then amounts to $\frac{1}{50}$ of the mean of the temperatures (absolute) above and below.

x .	ω^2 .	ω .	$10\sqrt{(x/\omega)}$.	$-\lambda/k$.	λ'/k .	Wave-length (metres).	Period (seconds).
10^{-6}	0.9980×10^{-8}	0.9990×10^{-4}	1.0005	0.998	0.998	7.0	21.2
10^{-5}	0.9615×10^{-8}	0.9806×10^{-4}	1.010	0.981	0.980	69.2	65.9
10^{-4}	0.7143×10^{-8}	0.8453×10^{-4}	1.088	0.850	0.841	597.0	180.0
10^{-3}	2.004×10^{-8}	0.4476×10^{-4}	1.495	0.470	0.425	3160.0	301.0

* Stokes, 'Camb. Trans.,' 1847, vol. 8, p. 441; 'Math. and Phys. Papers,' vol. 1, p. 197.

The fourth column gives the ratio of the frequency to that of waves of the same length on the surface of separation of two homogeneous liquids with the same discontinuity of density, as given by (123), viz., the ratio is

$$\frac{\sigma}{\sqrt{(gk) \cdot b/a}} = \frac{10\sqrt{x}}{\sqrt{\omega}},$$

on the present suppositions. The seventh column is calculated from $2\pi/k = 2\pi a^2 \omega/g$, taking $a = 332$ metres per second; and the last from $2\pi/\sigma = 2\pi a \omega/g\sqrt{x}$. It is seen that, with increasing wave-length, the wave-velocity tends more and more to exceed the value estimated on the assumption of the homogeneity and incompressibility of the two fluids. At the same time, the disturbance tends to become, relatively as well as absolutely, less and less concentrated in the neighbourhood of the plane of discontinuity.

14. In this question, again, it is of some interest to compare the case of waves on the common boundary of two liquids, each of which, though incompressible, has a similar gradation of density. We therefore write, in (86),

$$\frac{1}{\rho_0} \frac{d\rho_0}{dy} = q, \text{ a constant.} \quad (125)$$

If we assume that

$$\psi = Ce^{\lambda y}, \quad (126)$$

we derive

$$\lambda^2 + q\lambda + \left(\frac{qg}{\sigma^2} - 1\right)k^2 = 0. \quad (127)$$

These formulæ may be supposed to relate to the lower region; for the upper region we write q', λ', C' for q, λ, C , respectively.

The continuity of v involves, by (87), that of ψ , so that $C' = C$. Also, in virtue of the continuity of Dp/Dt , we have from (88)

$$\rho(\sigma^2\lambda + gk^2) = \rho'(\sigma'^2\lambda' + gk^2), \quad (128)$$

where ρ, ρ' , are the densities just below and just above the plane $y = 0$.

If the two fluids had been portions of the same gas at different temperatures we should have had

$$q = \gamma g/c^2, \quad q' = \gamma g/c'^2, \quad (129)$$

and therefore

$$\rho/\rho' = q/q'. \quad (130)$$

Now from (127) we have

$$q(\sigma^2\lambda + gk^2) = \sigma^2(k^2 - \lambda^2). \quad (131)$$

Hence, if we adopt the relation (130) for the sake of the comparison, we must have $\lambda^2 = \lambda'^2$, or, taking account of the signs, $\lambda = -\lambda'$. This leads to

$$\frac{\lambda'}{k} = -\frac{\lambda}{k} = \frac{q-q'}{q+q'} \cdot \frac{gk}{\sigma^2}, \quad (132)$$

and

$$\left(\frac{\sigma^2}{gk}\right)^2 - \frac{2qq'}{k(q+q')} \frac{\sigma^2}{gk} - \left(\frac{q-q'}{q+q'}\right)^2 = 0. \quad (133)$$

The positive root of this quadratic in σ^2/gk is to be taken, since it is the only one which gives the proper signs to λ, λ' , it being assumed that $\rho > \rho'$ and therefore $q > q'$. For infinitesimal values of q, q' , we reproduce the relations (123).

In order to make the variations of density follow exactly the same law as in the atmospheric problem of § 13 we must give to q, q' , the values (129). In the notation of (118), (119), we have then

$$x^2 - \gamma\omega^2 x - \omega^2 b^4/a^4 = 0. \quad (134)$$

The following table, like the former one, refers to the case of $b^2/a^2 = 1/100$. In order that the comparison may be for the same series of wave-lengths, those values of ω are chosen which were obtained in the previous numerical work. The significance of the column headed $10\sqrt{(x/\omega)}$ is the same as on p. 570. The comparison shows the usual effect of a constraint in increasing the frequency.

ω .	$10\sqrt{(x/\omega)}$.	λ'/k .	Wave-length (metres).	Period (seconds).
0.9980×10^{-4}	1.003	0.998	7.0	21.2
0.9806×10^{-3}	1.035	0.984	69.2	64.3
0.8452×10^{-2}	1.324	0.570	597.0	148.0
0.4476×10^{-1}	2.534	0.156	3160.0	178.0

*Sturm-Liouville Series of Normal Functions in the Theory of
Integral Equations.*

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(Abstract.)

In a memoir read before the Society on May 13 last I proved a theorem* which may be stated as follows:—

Let $\psi_1(s), \psi_2(s), \dots, \psi_n(s), \dots$ be a complete system of normal functions relating to a function $K(s, t)$ which is of positive type in the square $a \leq s \leq b, a \leq t \leq b$; and let $\lambda_1, \lambda_2, \dots, \lambda_n, \dots$ be the corresponding singular values. Then the series

$$\frac{\psi_1(s)\psi_1(t)}{\lambda_1 - \lambda} + \frac{\psi_2(s)\psi_2(t)}{\lambda_2 - \lambda} + \dots + \frac{\psi_n(s)\psi_n(t)}{\lambda_n - \lambda} + \dots$$

converges absolutely and uniformly, and has for its sum function $K_\lambda(s, t)$, the solving function of $\kappa(s, t)$.

I now show that this leads to the following theorem relative to the expansion of an arbitrary function as a series of such normal functions:—

Let the arrangement of the normal functions $\psi_1(s), \psi_2(s), \dots, \psi_n(s), \dots$ be such that the corresponding singular values are in non-decreasing order of magnitude; and let $U(s), L(s)$ be respectively the upper and lower limits of indeterminacy of the series

$$\psi_1(s) \int_a^b \psi_1(t)f(t) dt + \psi_2(s) \int_a^b \psi_2(t)f(t) dt + \dots + \psi_n(s) \int_a^b \psi_n(t)f(t) dt + \dots,$$

in which $f(s)$ is any function having a Lebesgue integral in the interval (a, b) . Then

$$U(s) \geq \overline{\lim}_{\lambda \rightarrow -\infty} -\lambda \int_a^b K_\lambda(s, t)f(t) dt \geq \underline{\lim}_{\lambda \rightarrow -\infty} -\lambda \int_a^b K_\lambda(s, t)f(t) dt \geq L(s) \quad (1)$$

It will be clear that the application of this theorem in any particular case requires the determination of an asymptotic formula for $K_\lambda(s, t)$ when λ is negative and numerically great. In the third section I proceed to obtain such a formula for the case in which $\kappa(s, t)$ is the Green's function of the equation

$$\frac{d^2 u}{ds^2} + qu = 0$$

* Vide 'Phil. Trans. Roy. Soc.,' Series A, vol. 209, p. 445.

for an assigned pair of boundary conditions at the end points of $(0, \pi)$. The only restriction placed upon the function of s denoted by q is that it should be continuous in $(0, \pi)$. By employing this formula I show that, if $f(s)$ is any function which has a Lebesgue integral in $(0, \pi)$

$$\overline{\omega(s)} \geq \lim_{\lambda \rightarrow -\infty} -\lambda \int_0^\pi K_\lambda(s, t) f(t) dt \geq \lim_{\lambda \rightarrow -\infty} -\lambda \int_0^\pi K_\lambda(s, t) f(t) dt \geq \underline{\omega(s)}, \quad (2)$$

where $\overline{\omega(s)}$ and $\underline{\omega(s)}$ are respectively the upper and lower bilateral limits of $f(s)$ at a point s of the open interval $(0, \pi)$. These bilateral limits are defined as follows. Let $\chi_r(t)$ ($r = 1, 2$) be any two functions which possess limited second derivatives in an interval $(0, \alpha)$ ($\alpha > 0$), and are such that

$$\chi_r(0) = 0, \quad \chi'_r(0) = 1.$$

The upper limit of

$$f(s - \chi_1(t)) + f(s + \chi_2(t)), \quad (3)$$

as t tends to zero, will, in general, assume different values as the functions $\chi_1(t)$, $\chi_2(t)$, are varied. The lower limit of these values is called the *upper bilateral limit* of $f(s)$ at the point s . Similarly, the upper limit of the values assumed by the lower limit of (3) is defined to be the *lower bilateral limit* of $f(s)$ at s .

In the case before us, the normal functions $\psi_1(s)$, $\psi_2(s)$, ..., $\psi_n(s)$, ... are the solutions of

$$\frac{d^2 u}{ds^2} + (q + \mu)u = 0,$$

which, for $\mu = \lambda_1, \lambda_2, \dots, \lambda_n, \dots$, satisfy the same pair of boundary conditions as $\kappa(s, t)$. The series

$$\psi_1(s) \int_0^\pi \psi_1(t) f(t) dt + \psi_2(s) \int_0^\pi \psi_2(t) f(t) dt + \dots + \psi_n(s) \int_0^\pi \psi_n(t) f(t) dt + \dots$$

is called a *canonical Sturm-Liouville series corresponding to $f(s)$* . It follows from (1) that we have

$$U(s) \geq \lim_{\lambda \rightarrow -\infty} -\lambda \int_0^\pi K_\lambda(s, t) f(t) dt \geq \lim_{\lambda \rightarrow -\infty} -\lambda \int_0^\pi K_\lambda(s, t) f(t) dt \geq L(s)$$

at each point of $(0, \pi)$. This, in conjunction with (2), enables us to state general theorems relative to the behaviour of canonical Sturm-Liouville series. Thus, defining the common value of the upper and lower bilateral limits at a point where they are equal to be the bilateral limit at that point, we have:—

At each point of the open interval $(0, \pi)$ where $\omega(s)$, the bilateral limit of $f(s)$, exists

$$U(s) = \omega(s) = L(s).$$

Again, taking the case in which $U(s) = L(s)$, we see that:—

The sum of a canonical Sturm-Liouville series corresponding to $f(s)$ at any point of the open interval $(0, \pi)$ where it converges lies between the upper and lower bilateral limits of $f(s)$ at the point.

¶ In the later portions of this section these theorems are extended to the most general type of Sturm-Liouville series (§ 22, *et seq.*).

In the fourth section I consider the convergence of canonical Sturm-Liouville series, employing a method which is suggested by the proof of the theorem of II, § 4, and the asymptotic formula obtained at the commencement of the third section.

It is eventually shown that:—

At any point of the open interval $(0, \pi)$ each of the canonical Sturm-Liouville series corresponding to an assigned function which is integrable in $(0, \pi)$ in accordance with Lebesgue's definition has the same limits of indeterminacy.

In particular we have:—

If any one of the canonical Sturm-Liouville series corresponding to the function converges at a point of the open interval $(0, \pi)$, then all of them converge at this point, and all have the same sum.

It is also shown that:—

If any one of the canonical Sturm-Liouville series corresponding to the assigned function converges uniformly in a set of points which together with its limiting points is contained within $(0, \pi)$, then all of these series converge uniformly in the set.

From the two theorems just quoted sufficient conditions are obtained for the convergence and for the uniform convergence of these series. Finally, the corresponding results are obtained for the general Sturm-Liouville series.

Conduction of Heat through Rarefied Gases.—II.

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(Received August 25,—Read November 10, 1910.)

In a previous paper* measurements were described of the thermal conductivity of twelve different gases in what may be termed a "free-path vacuum," that is, at pressures so low that the molecules conducting the heat from the hot to the cold surface do not, as a rule, experience mutual encounters. It was shown that at sufficiently low pressure the conductivity of all the gases was proportional to the pressure, and the conductivity K (defined as the calories dissipated per second, per 0.01 mm. pressure of gas per square centimetre of hot surface, per 1° difference of temperature between the latter and its surroundings) was compared with the theoretical conductivity Q , as calculated approximately from the molecular heat and mean molecular velocity of the gas, by means of the kinetic theory, on the assumption that the heat interchange between the molecule and the surface it impinges upon was perfect. For argon and neon the ratio K/Q (1.09 and 1.04 respectively) was in gratifying agreement with this assumption, but for all the other gases the ratio was less than unity. For these the ratio was greater than 0.66, except for helium and hydrogen, for which the very low values 0.5 and 0.25 respectively were found. The suggestion was hazarded that possibly for these light gases the interchange of heat is imperfect, owing to the greater velocities at which the molecules move.

In the present paper some of the earlier measurements have been repeated with the original apparatus, with better provision for keeping the temperature of the surrounding water jacket uniform. Then the apparatus was rebuilt to allow of the measurements of the conductivity to be taken over a wide range of temperature, both of the hot and cold surface, and the effect of variation of the temperature on the ratio K/Q was examined. Measurements were confined to the three gases—hydrogen, helium, and argon. Incidentally the effect on the conductivity of hydrogen of using a hot palladium surface instead of one of platinum was examined. The result of these new experiments has been to negative the suggestion already referred to, that the discrepancies between the found and calculated conductivities might be due to imperfect interchange of energy on impact. The ratio K/Q appears to diminish as the temperature at which the experiments are

* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 254.

performed decreases and to increase as the temperature is increased, and no explanation of this can at present be suggested.

Experiments with the Original Apparatus.—The conductivities of helium, argon, neon, and hydrogen were redetermined by the original method and apparatus. In the whole of the work to be described the water round the apparatus was kept at nearly constant temperature by first circulating through a considerable length of metal tubing immersed in a thermostat, usually at 24°. The values of K and of K/Q are shown in Table I, together with the results obtained previously. They agree fairly well with the results already given, that of hydrogen being slightly higher.

Table I.—Original Apparatus. Strip at 61°.

Gas.	New determinations at 22°.			Old determinations at ca. 15°.		
	$K \times 10^6$.	$Q \times 10^6$.	K/Q .	$K \times 10^6$.	$Q \times 10^6$.	K/Q .
Helium	1.99	3.75	0.53	1.94	3.80	0.51
Neon	1.78	1.68	1.06	1.76	1.70	1.04
Argon.....	1.32	1.18	1.12	1.30	1.20	1.09
Hydrogen	2.90	8.85	0.33	2.29	8.95	0.25

Further experiments were then carried out on helium and argon, but the strip was now heated to different temperatures. The electrical arrangements were also somewhat modified. The two ratio arms of the bridge were two 1-ohm coils of stout Eureka wire. The other arm of the bridge was a set of variable resistances of the same material, so that the strip could be heated to various known temperatures. In measuring the fall of potential along the strip, an Elliot voltmeter, with an 8-inch dial reading from 0 to 2.5 volts, was permanently connected across the potential leads. To compensate for the resistance of this instrument, an equal resistance (389 ohms) was put in parallel with the corresponding arm. In this series the variable resistance was set so that at the balance point the strip should assume temperatures corresponding with the following:—water at 22°, the boiling points of the following liquids, ether 33°·6, water 100°, ethylene dibromide 130°, and aniline 195°.* This was accomplished with the apparatus filled with hydrogen and jacketed at the desired temperature, by altering the variable resistance until balance was obtained with a momentary feeble current. The resistance of the strip at the working temperature was found

* This temperature was assumed from the resistance of the strip, which was found to be a linear function of the temperature. It is probable that the boiling-point of the aniline had been raised by decomposition.

by reading the fall of potential across the potential leads when balance was produced with a known heating current, the walls of the apparatus being cold. The results are included in Table II. They showed that but little change in

Table II.—Original Apparatus. Temperature of Strip varied.

Gas.	Temp. of bath.	Temp. of strip.	Difference.	$K \times 10^5$.	$Q \times 10^5$.	K/Q .
Helium	°	°	°			
	Ca. 6	33·6	27·6	1·86	3·86	0·48
	23·3	61	37·7	1·99	3·75	0·53
	22	130	108	2·08	3·75	0·55
Argon	22·5	195	172·5	2·06	3·75	0·55
	Ca. 6	33·6	27·6	1·28	1·22	1·05
	22·8	61	38·2	1·32	1·18	1·12
	22	100	78	1·54	1·18	1·30
	22	130	108	1·38	1·18	1·16
	22	195	173	1·37	1·18	1·16

the ratio K/Q was produced by changes in the difference of temperature between strip and wall from 27° to 173° , the temperature of the wall being always about 22° . The low conductivity of argon and the comparatively small range over which its conductivity is a linear function of the pressure make the determination of the ratio less accurate than for helium or hydrogen. For helium the ratio K/Q remained sensibly constant over the range examined. This was unexpected. On the view suggested tentatively to account for the smallness of the ratio, that perfect interchange of energy is not secured with the faster moving molecules by a single impact, it is to be expected that the ratio would decrease as the temperature of the strip was increased.

Comparison of the Conductivity of Hydrogen with Heated Surfaces of Palladium and Platinum.—On the same view it had been deduced, since hydrogen is occluded by heated palladium more than by platinum, that the value of K for hydrogen should be greater for a heated palladium surface than for one of platinum. The point was simply tested in the following way:—The apparatus employed consisted of two parallel tubes carrying, axially, similar wires of platinum and palladium respectively. The tubes were joined together at their upper extremities and immersed in the thermostat, in order that the same gas might be investigated under identical conditions of temperature and pressure. The two wires formed two arms of a bridge, the rest of the bridge consisting of a stretched wire along which a sliding contact moved. A sensitive galvanometer was inserted between the slider and the two ratio arms of the bridge. Care was taken to avoid

heating the wires to such an extent as to cause them to touch the sides of the tubes. Argon and hydrogen were investigated by this apparatus. Experiments were performed in water at 22° , and also with the apparatus cooled in a mixture of solid carbon dioxide and ether giving a temperature of about -78° . Both gases were investigated over a fairly wide range of pressure, and the behaviour with both was absolutely identical, so far as could be seen. The balance point remained at the middle of the bridge wire, only moving to a very slight extent as the pressure of the gas became reduced, due to a slight difference between the temperature coefficients of resistance of the platinum and palladium wires. These experiments, therefore, negative the prediction that hydrogen may be expected to exhibit a higher thermal conductivity when tested with a surface of palladium than with one of platinum.

Experiments with the Rewilt Apparatus.—A new tube, with the platinum strip employed in the original apparatus, was made up in a form suitable for work at low temperatures. To allow for expansion and contraction of the strip with change of temperature, a spiral spring of hard copper wire was employed at the top, instead of a weight at the bottom as in the original apparatus. But since the resistance of this spring was a considerable fraction of that of the platinum strip, it was no longer possible to work with the strip as one arm of a Wheatstone bridge. The diameter of the new tube was very nearly the same as the old one; it was actually 0.97 cm., and the potential leads were 41.1 cm. apart. One of the original set of determinations that had been made with the old apparatus was repeated as closely as possible with the new, and the curves obtained were practically identical, showing that the electrical properties of the strip were unchanged.

The method of working was as follows:—The strip, with its potential leads connected with the voltmeter, was put in series with a constant resistance of stout Eureka wire (shunted with the resistance of 389 ohms, equal to that of the voltmeter), of such a value as to be equal to the resistance of the portion of the strip between the potential leads at the desired working temperature, and with a rheostat for adjusting the heating current till this equality was obtained. Adjustment was made by the use of a commutator, which exchanged the voltmeter and the similar 389 ohms resistance. The rheostat was then simply adjusted until the voltmeter readings were constant for the two positions of the commutator. With the apparatus surrounded by liquid air, the strip was worked at two temperatures, (1) at -120° C., and (2) at -75° C. Helium and hydrogen were investigated at both temperatures.

The resistance of the strip between the potential leads was carefully determined at liquid air temperature and in a bath of solid carbon dioxide and ether. This was done by observing with a potentiometer the fall of potential

across the potential leads of the strip, produced by a known momentary feeble current, when the apparatus was filled with hydrogen and immersed in the cooling bath. It was found that the resistance of the strip was very nearly a linear function of the temperature from -185° to 261° . At low temperatures the linear portion of the curve, expressing the relation between the heat dissipated and the pressure of the gas, is curtailed, and it was not found possible for this reason to work at low temperatures with argon, but experiments were done with hydrogen and helium. The results are given in Table III.

Table III.—Rebuilt Apparatus immersed in Liquid Air.

Gas.	Temp. of strip.	Difference.	$K \times 10^4$.	$Q \times 10^4$.	K/Q .
	°	°			
Helium	-120	65	2.55	6.87	0.37
	- 75	110	2.55	6.87	0.37
Hydrogen	- 75	110	3.10	16.2	0.19

From the expression before deduced,

$$Q = \frac{1}{6} \frac{n}{N} HG, *$$

in which H and N are constants, while G varies directly as the square root of the absolute temperature and n inversely as the absolute temperature, it follows that Q varies inversely as the square root of the absolute temperature.

It had been deduced that the value of K/Q for helium at liquid air temperature should approach unity, since at that temperature its molecular velocity is similar to that of neon at room temperature. The ratio K/Q for both helium and hydrogen was, however, found to be distinctly *smaller* at low temperature. As before, variation of the difference of temperature between the wall and the strip appeared to make little, if any, difference. In these low-temperature measurements the radiation loss was negligible.

Further experiments were then performed with the apparatus jacketed with steam and the strip at 195° in one set, and 264° in another, and with the apparatus jacketed with aniline and the strip at 264° .

In the experiments at higher temperatures, the radiation loss became of considerable importance. It was determined in each case by extrapolating

* Where H is the molecular heat at constant volume, G the mean molecular velocity, n the number of molecules in 1 c.c. of gas at the temperature of the wall and 0.01 mm. pressure, and N the number in the gram-molecule.

the curves to zero pressure, except in the experiment with the strip at 264° and the bath at 100° . For this case the separate curves did not give a sufficiently concordant result, and the loss was determined directly in a calcium vacuum. In attempting to push the temperature higher by jacketing with sulphur vapour heated in a quartz tube, the copper wire spring softened, and the apparatus was rendered useless. The results are shown in Table IV.

Table IV.—Rebuilt Apparatus. High Temperatures.

Gas.	Temp. of bath.	Temp. of strip.	Difference.	$K \times 10^6$.	$Q \times 10^6$.	K/Q .
Helium	°	°	°			
	100	195	95	2.03	3.34	0.61
	100	264	164	1.65	3.34	0.50
Hydrogen	187	264	77	2.06	3.01	0.68
	100	195	95	2.45	7.85	0.31
	100	264	164	1.88	7.85	0.24
Argon	100	195	95	1.75	1.06	1.65
	100	264	164	1.21	1.06	1.14
	187	264	77	1.36	0.95	1.43

For convenience, the whole of the results are collected for each gas separately in Table V. The measurements are arranged in ascending order of bath temperature, the different measurements at the same bath temperature being arranged in ascending order of strip temperature. It appears that rise in temperature of both surfaces causes the ratio K/Q to increase, while an increase in the difference of temperature between wall and strip causes it to diminish. Helium is perfectly in accord with this view, and so is hydrogen, though here only four measurements have been done. For argon, also, the results, although they appear at first sight irregular, are not inconsistent with the view that two opposing influences are at work, and sometimes the one and sometimes the other predominates.

It is clear, from the fact that a value as high as 1.65 for K/Q has been obtained for argon, that this gas conforms to theory hardly better than the others, and that the agreement between the theoretical and experimental values found for it in the last paper was partly fortuitous. The reasons for the discrepancy between the theory and the experimental results remain unexplained. Admittedly, the theory, which assumes all the molecules to possess the temperature of the wall, is imperfect, but it may be questioned whether this can make any very serious difference in the calculated values. It is interesting to note that the conductivity found

for gases at low pressure varies far less with the nature of the gas and with the temperature than is to be expected from kinetic considerations. Thus the extreme values of K found in these experiments are 1.2 and 3.1, whereas the extreme values of Q over the same range are 0.95 and 16.2.

Table V.—Collected Results.

Temp. of bath.	Temp. of strip.	Difference.	$K \times 10^3$.	K/Q .	K/Q corrected (see Addendum).
Helium.					
-185	-120	65	2.55	0.37	0.49
-185	-75	110	2.55	0.37	0.49
6	38.6	27.6	1.86	0.48	0.36
23.3	61	37.7	1.99	0.53	0.38
22	130	108	2.08	0.55	0.39
22	195	173	2.06	0.55	0.39
100	195	95	2.03	0.61	0.39
100	264	164	1.65	0.50	0.32
187	264	77	2.06	0.68	0.39
Hydrogen.					
-185	-75	110	3.10	0.19	0.25
21	61	40	2.90	0.33	0.24
100	195	95	2.45	0.81	0.19
100	264	164	1.88	0.24	0.15
Argon.					
6	38.6	27.6	1.28	1.05	0.78
22	61	39	1.32	1.12	0.80
22	100	78	1.54	1.30	0.93
22	130	108	1.38	1.16	0.83
22	195	173	1.37	1.16	0.83
100	195	95	1.75	1.65	1.05
100	264	164	1.21	1.14	0.72
187	264	77	1.36	1.43	0.83

Addendum, October 15, 1910.

Sir Joseph Larmor has called our attention to some recent papers by M. Knudsen on the dynamics of rarefied gases which reveal a source of error

in the foregoing measurements of the pressure of the gas. First, we may be allowed to state that we had already considered the measurements of the pressure to be the least satisfactory, and had decided, if an opportunity of continuing the work arose, to do away altogether with the pressure gauge. This could readily be done by having the tube containing the hot strip, the volume of which was determined once for all, connected by capillary tubing with a definite volume enclosed between two taps, arranged for admitting a definite quantity of any gas to the apparatus. By exhausting the apparatus with calcium at the start and measuring the heat dissipation after each admission of one such quantity of gas, the experimental work would be much simplified and the results more definite. For in a previous paper* it has been pointed out that when the free path of the molecule becomes comparable with the diameter of the connecting tube there is, properly speaking, no pressure in the hydrostatic sense, since flow does not operate to equalise the concentration. It was stated that under these conditions "gauge readings of pressure in apparatus connected to the gauge by a narrow orifice are not, strictly, pressure readings at all." Knudsen† has deduced from the kinetic theory that between two closed vessels at different temperatures containing the same gas, and connected by a tube, of diameter small compared with the mean free path of the gas molecule, there must exist a difference of pressure, given by

$$p_1/p_2 = \sqrt{T_1/T_2}$$

where p_1 , T_1 , and p_2 , T_2 , are the pressures and temperatures of the two vessels respectively. In fact, Osborne Reynolds, in work on thermal transpiration, had, long previously, arrived at the same relation.‡ Knudsen brings in support of this remarkable deduction many striking experiments, and there can be little doubt that some common physical measurements, as well as those discussed in the foregoing pages, are vitiated by this effect.

In the foregoing measurements, with the tube containing the heated strip jacketed at high and low temperatures, the pressure readings of the gauge, which remained at room temperature, would not represent the real pressures in the tube. Although the connecting tubing was some 3 or 4 mm. wide, yet this was always small compared with the mean free path of the gas molecules. As there seems to be no reason why the above relation cannot be exactly applied to our experiments, we have corrected the ratio, K/Q , given in Table V, by multiplying it by $\sqrt{T_1/T_2}$, where T_1 is the absolute temperature

* F. Soddy and T. D. Mackenzie, 'Roy. Soc. Proc.,' 1908, A, vol. 80, p. 102.

† "Eine Revision der Gleichgewichtsbedingung der Gase," 'Annalen der Physik,' 1910, vol. 31, 205.

‡ 'Phil. Trans.,' 1879, p. 727.

of the room, assumed throughout to be 17° C., and T_s the absolute temperature of the bath. The values so corrected, and multiplied by the factor 0.724 described below, have been added in italics as another column to Table V. It will be seen that the results now have quite a different appearance, not unfavourable to the original hypothesis of incomplete interchange of energy on impact. For helium, the value of K/Q is distinctly higher at liquid air temperature than at room temperature, but remains almost constant from room temperature up to 187° . The low value with the bath at 100° and the strip at 264° is exceptional. For hydrogen, the value of K/Q is also highest at the lowest temperature, and falls regularly, so far as can be seen, with increasing temperature. Argon is still somewhat irregular. Over the range investigated, 6° to 187° , temperature appears to have little influence. As already remarked, these results are probably not so accurate as those with the other gases.

Finally, reference must be made to a recent paper by M. Smoluchowski,* who, in the last section of his paper, deals with the results obtained by us in our first paper, from the theoretical standpoint. He gives an exact calculation for the conduction of heat in a rarefied gas on Maxwell's assumption that some of the impinging molecules are reflected with their original velocity, while others are emitted with a new velocity corresponding to the temperature of the surface. He points out that in our roughly calculated formula for Q , the numerical factor should be $1/\sqrt{6\pi}$ instead of $1/6$, so that all our values for K/Q should be multiplied by the factor $\sqrt{\pi/6} = 0.724$.† In addition, the value of Q , to correct for imperfect equalisation of the mean energy of the impinging molecules to that of the molecules in the wall, must be multiplied by the factor $(1-\beta)/(1+\beta)$, where β is derived from the formula

$$s - \theta_0 = \beta(\theta_m - \theta_0),$$

in which θ_0 , θ_m , and s denote the temperature of the wall, of the impinging and of the emitted molecules. With only the first correction in the values of K/Q , this ratio ranges for the 12 gases examined from 0.79, for argon, to 0.18 for hydrogen, showing that the interchange of energy is always imperfect. Smoluchowski does not discuss the interesting question as to how this coefficient β is likely to vary with the velocity

* "Contributions to the Theory of Transpiration, Diffusion, and Thermal Conduction in Rarefied Gases," 'Bull. International de l'Acad. des Sciences de Cracovie,' 1910, A, No. 7, p. 295.

† Prof. Larmor had sent me the same correction as M. Smoluchowski's, remarked to him independently by Mr. Sydney Chapman. A slight change has been made in the decimal value of the factor.

or temperature of the molecule. He considers our earlier results to range very much as is to be expected, the interchange of energy with the molecules of the platinum wall being less perfect for the lighter gas molecules than for heavier ones, and also for polyatomic than for monatomic, for the reason that intramolecular energy is less disposed to equalisation by impacts than energy of progressive motion.

It is clear that further experimental work must be done in the manner suggested before the necessary data are available. The experiment on the conduction of hydrogen with palladium and platinum wires tells against the idea of imperfect interchange of energy, but it is by no means conclusive. Moreover, Prof. Larinor remarks that the recent experiments of Millikan on electrified water drops in an electric field, when interpreted by the formula of E. Cunningham,* make β very small, so that, for air on water at any rate, little correction of that kind arises.

*An Electrostatic Voltmeter for Photographic Recording of
Atmospheric Potential.*

By GEORGE W. WALKER, A.R.C.Sc., M.A., Superintendent of Eskdalemuir
Observatory.

(Communicated by Dr. W. N. Shaw, F.R.S. Received October 11,—
Read November 24, 1910.)

The difficulties attending continuous registration of electrical potential gradient of the atmosphere are very great; but it is not my intention in this paper to discuss these. My object is to call attention to the measuring part of an electrograph, and more especially to experiments made with an instrument that promises to be of considerable service in work of this kind. A recording voltmeter ought to have a uniform scale value over the range for which it is intended to be used, it must possess a high degree of insulation, and it ought to be capable of acting efficiently for long periods without having to be taken to pieces for cleaning. The general excellence of the Dolezalek electrometer and its high degree of mechanical symmetry suggested to me its use as a recorder, although I do not know that it has been tried before.

The instrument was designed to measure very small differences of potential

* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 109.

between the quadrants with a potential of, say, 100 volts on the needle. The first thing to ascertain was whether, with a fixed difference due to a single Weston cell, the sensitiveness could be reduced so that the movement of the needle would record, on a suitable scale, the potential applied to it. A trial suspension made of phosphor bronze proved successful, and a scale value of about 200 volts per centimetre was obtained on the photographic paper, which is carried on a drum 1 metre from the mirror attached to the needle. Up to 500 or 600 volts the behaviour was excellent, but for higher potentials the needle began to tilt, and if a sudden change was made the needle generally discharged to the quadrants. Experience showed that it would have frequently to carry over 1000 volts. The needle was therefore loaded by prolonging the vertical axis to about 3 cms. beneath the needle, and adding at the end a small brass nut of about $1\frac{1}{2}$ gm. It now carries 1100 volts with perfect safety and stability.

The loading reduced the sensitiveness, and I now use three Weston cells and obtain a scale value of about 115 volts per centimetre on the paper. As far as I can test with a high potential Wulf electrometer, the scale value is constant to within 2 or 3 per cent. over the range of the sheet, which is about 900 volts + or -. It requires a little care and patience to adjust the instrument to symmetry over this large range of 1800 volts.

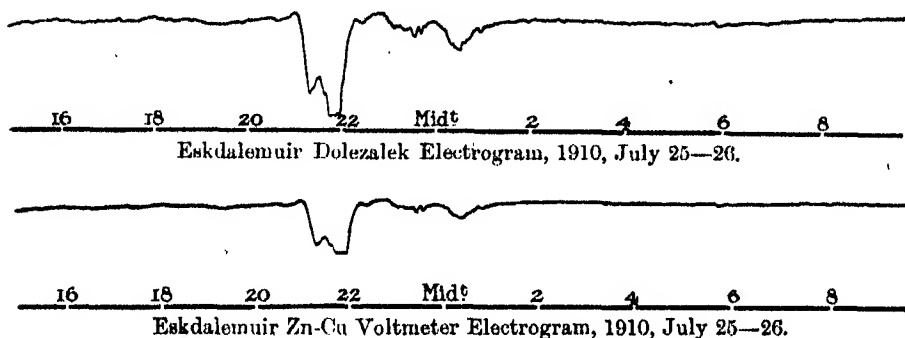
The present scale value is suitable for ordinary days, but in stormy weather it is too large. We therefore require a second voltmeter working at a lower sensitiveness in order to get a complete record. From what has been said, it is clear that a Dolezalek with one Weston cell would serve admirably. It may be mentioned that although the instrument is not dead-beat at this sensitiveness, the needle comes to rest long before the collecting water-jet responds to change of potential, but discussion of this point is reserved for another occasion.

Meanwhile experiments in another direction have been carried on. Some ten years ago Mr. W. G. Pye made for me an experimental voltmeter, in which I proposed to rely on the contact difference of potential between zinc and copper to give a couple on a suspended electrometer needle. Two circular plates were made up of alternate 90° sectors of zinc and copper, soldered together at the junctions, and the two plates were set parallel by means of a circular copper ring, thus completing the "box quadrant" arrangement.

I was satisfied some years ago that the instrument could be adjusted to give quite reliable readings for a steady potential on the needle. When the question of having a second recorder for high potentials arose, it occurred to me to ascertain if the zinc-copper voltmeter would do. The old plates

were accordingly looked out, and, although they had been damaged and repaired some years ago, an instrument was made up in the observatory workshop, closely resembling the Dolezalek in general features, although equal mechanical accuracy was impossible in the circumstances.

When connected to the Dolezalek and collecting system, the photographic records from the two instruments were perfectly similar. Fig. 1 is a reproduction of a specimen record.



It proved fairly easy to adjust the new instrument to uniform scale value (about 290 volts per centimetre) over a range of 400 or 500 volts + or - ; but for greater potentials I found considerable difficulty. This arose simply from the lack of perfect mechanical symmetry in the instrument, but with patience I finally succeeded in getting practical uniformity up to 1100 volts + or -.

I think these results, obtained with a "home-made" instrument, warrant the making of a new one, which shall equal in mechanical precision the Dolezalek electrometer, and so admit of easier adjustment. At present the needle is not sufficiently damped for very rapid changes, but this can be overcome by using a Dolezalek needle or by electromagnetic damping.

The instrument possesses an obvious advantage for recording work, as insulation of the quadrants is unnecessary. The only part requiring good insulation is the head for carrying the needle. This may be done with amber, but we avoided the expense and got quite as good a result by moulding a sulphur bush.

The question of a cheap and efficient insulator is strictly beyond the scope of this paper; but as we have obtained most satisfactory results by using sulphur, I have been advised to refer to the matter.

It is practically impossible to work sulphur in the ordinary mechanical way, and resort must be had to moulding. For this purpose a carefully cleaned glass tube or test-tube of the required diameter is used. Ordinary

roll sulphur is then melted in a clean porcelain dish, and it is essential that the temperature should be just sufficient to melt the sulphur and no more. The slightest darkening of the liquid is fatal to a good result. The molten sulphur is run into the glass tube and allowed to set for 24 hours. It may then be taken out, and usually the test-tube has to be sacrificed in the process. Initially the rod insulates magnificently, but in the course of a few days it gets defective. If, however, the glossy surface is then removed by light rubbing with fine sand-paper, the insulating power is recovered and maintained. I cannot yet say how long this will last, but I have some pieces in use that have not been touched for over six months, and they insulate now as well as they did originally and quite as well as amber. I have made special tests in very damp weather without finding any failure of the sulphur. If the support has to stand any strain it may be fitted into a brass socket with a piece of thin paper. Five such supports, 1-inch diameter, carry our copper tank, which is 3 feet in diameter and 6 inches deep and filled with water. An idea of the insulation may be obtained from the fact that when electrified the tank falls to $1/e$ of its original potential in from 50 to 60 minutes normally.

I have found that sulphur moulded directly into brass or copper tube gradually deteriorates, and on breaking the sulphur it is found to contain dark streaks of what I presume is copper sulphide. If, however, the brass is first lined with thin paper the sulphur maintains its insulating power for months without any sign of deteriorating.

It is important not to touch the sulphur with fingers at all greasy. If occasion arises to remove a spider's thread, it is best to do so with a piece of fine sand-paper or even a piece of fine tissue paper.

Mr. Black, the observatory mechanic, has greatly assisted me in ascertaining what precautions are necessary to make sulphur a serviceable insulator in laboratory work.

[*Note added December 8.*—Zinc-copper couples have been used before by Lord Kelvin and by Prof. C. V. Boys.* Sulphur insulation, with the remarkable efficiency of which this paper is concerned, has also been advocated by Mr. C. T. R. Wilson, by Dr. Threlfall, and by Prof. Le Cadet.†]

* 'Electrician,' 1896.

† 'Annales de l'Université de Lyon,' 1898, vol. 35, p. 32.

The Measurement of End-Standards of Length.

By P. E. SHAW, B.A., D.Sc.

(Communicated by Prof. Poynting, F.R.S. Received November 18, 1910,—
Read January 12, 1911.)

During the last few years there have been improvements in this branch of metrology. In 1905, as pointed out by the writer,* the best gauges were greatly defective as to their end faces and the machines for their measurement were faulty in principle. Since then Johanson has, by a secret process, produced gauges incomparably superior to anything previously on the market, with the result that other gauge-makers have been stimulated to improve their standards.

The ordinary bar gauge has flat ends. This paper deals with this form only. The ideal gauge would satisfy two conditions: (1) The ends to be absolutely plane and parallel, though they need not be truly normal to the length of the bar; (2) the distance between the planes to be exactly the length for which the gauge stands. In this paper only condition (1) is considered.

Testing work too extensive for full publication has been performed, but the following brief account shows some improvements effected both in gauges and in measuring machines.

The method of measuring is fully described in the above paper. In brief, the machine consists of a massive bed carrying two measuring headstocks and a table for carrying and adjusting the gauge. The headstocks each carry a horizontal micrometer screw, working parallel to the bed, and a nut with a graduated head. These measure the bar, which rests on and is clamped to the table.

In taking a measurement the left screw, say, is brought into electric contact with the gauge, then the right screw is brought into electric contact with the gauge, and when the current passes through the gauge from one measuring point to the other, the two divided heads are read. The difference in the readings is a measure of the distance through the gauge from one measuring point to the other. In addition to the usual precautions against temperature changes provision is made to avoid shaking by arranging that the graduated heads are not actually touched by hand, but are worked by a hand pulley and string.

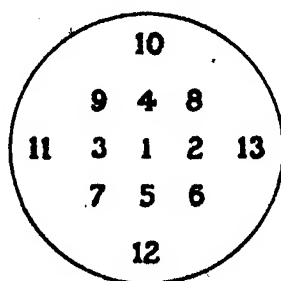
There are two novelties in this method of measuring: (1) the measurement is made electrically between point and point instead of between rough plane

* See 'Roy. Soc. Proc.,' A, 1906, vol. 77.

and rough plane; (2) the gauge can be moved, after a measurement in one position, into another parallel position at a known distance away and a new measurement taken. Thus the two gauge faces are simultaneously explored and errors become manifest.

Improvements in Gauges.

Suppose the face of the gauge is circular. Take 13 places equi-spaced as shown on the face. The first measure is taken from the centre of the face along a line normal to the face to the other face. The second measure is taken from point 2 along a parallel line, and so on for 13 measurements.



Since the gauge face generally slopes away from the centre in all directions, the centre is a place corresponding to maximum length through the gauge, and we should expect to find the greatest irregularities for the larger numbers, 10, 11, 12, 13, approaching the edge of the face. Such, in general, is the case.

The accompanying curves (fig. 1) show at a glance that the measures taken are very unequal for curves A, B, C, D, and less so for E, F, G.

One curve is produced from the measurements as above explained; the gauge is then reversed, and the twin curve produced. This is the procedure for curves A, B, C, E, F.

The small vertical divisions on the paper imply $0.5 \mu (= 1/2000 \text{ mm.})$; the horizontal divisions are arbitrary, but the whole length of curve represent generally about 6 mm. Thus the irregularities of the pair of gauge faces are exaggerated 400 times.

Let Δ = the arithmetic mean of the differences for all the readings at one time.

Let δ = the arithmetic mean of the differences in the readings for any one place. Thus Δ and δ give respectively measures of the accuracy of the gauge and of the machine. During the experimental work temperature changes may effect the length of the gauge. This would increase δ and, to a less extent, Δ .

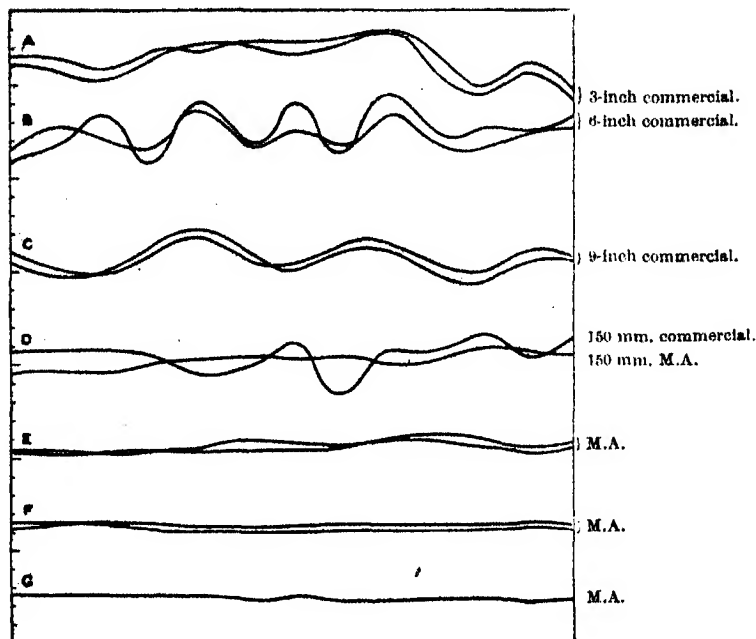


FIG. 1.

If both gauges and machine were perfect the curves in fig. 1 would be horizontal straight lines, whereas if the gauge alone were perfect the curves would be sinuous on account of the uncertain action of the machine. The lower curves in the figure approximate to the conditions of perfection, whereas the upper ones are very sinuous.

A. This represents readings on a 3-inch commercial gauge, measured direct and reverse.

$$\Delta = 3.6 \mu, \quad \delta = 0.4 \mu.$$

B. A 6-inch commercial gauge, direct and reverse.

$$\Delta = 3.2 \mu, \quad \delta = 0.8 \mu.$$

C. A 9-inch commercial gauge. This shows an advance in accuracy, the machine is much more true than the gauge.

$$\Delta = 2.6 \mu, \quad \delta = 0.4 \mu.$$

D. A comparison between a 150 mm. commercial gauge which has $\Delta = 3.5 \mu$ and a much better one, marked M.A., for which $\Delta = 1.0 \mu$. (This gauge and those used for curves E, F, G, were kindly made for the writer by Messrs. Manlove, Alliott, Ltd., Nottingham, who took much trouble during these experiments to perfect a lapping method of their own.)

E. This is a good gauge marked M.A.

$$\Delta = 1.0 \mu, \quad \delta = 0.5 \mu.$$

F. Another special gauge marked M.A. After taking a set of readings giving one curve, the gauge was re-lapped, measurements repeated, and the second curve produced.

$$\Delta = 0.6 \mu, \quad \delta = 0.4 \mu.$$

G. A mild-steel gauge. This is the best curve produced so far.

The commercial gauges mentioned are made by various well-known firms, whose names cannot, of course, be given; the gauges had been in sound keeping since they came from the makers, and were in a state of good preservation, so that the tests are fair.

From the above experimental curves and figures it is obvious that (1) it is possible to make far better gauges than those commonly issued as standards; (2) the best gauges so made are so nearly perfect in form that such errors as are found may be due to the imperfect working of the measuring machine and not to the gauge itself.

Improvement in the Measuring Machine.

At this juncture it seemed advisable to improve the machine. The table carrying the gauge was the chief source of error.

It is very difficult to provide a reliable mechanism for translating the gauge parallel to itself. Any looseness or rotation occurring during this translation will introduce errors in the measurements.

The table, as described in the former paper, was discarded. In its place is one involving a different principle. There is a plane surface plate set perpendicular to the bed. The plate on which the gauge rests is pressed by springs so as to rest against the surface plate, touching it at three points. If the surface plate is true and rigid, and the three feet remain always pressed against it, the movements of the gauge resting firmly on the plate must be strictly parallel. The surface plate is set perpendicular to the run of the bed by an optical arrangement.

The Johanson gauges are made in slabs, the cross-section in all cases being 35 mm. \times 10 mm. They are used singly or composite; in the latter case two or more are wrung together with pressure so as to adhere, and form a rigid composite gauge equal to the sum of the component parts. Whether single or composite these gauges were known to be very accurate, but it was hoped that with the improved measuring machine as described, any irregularities could be detected.

The following tables are typical of results found:—

Johanson Gauges.

2-inch single.			2-inch composite $\begin{cases} 0.850 \text{ inch.} \\ 0.450 \text{ " } \\ 0.700 \text{ " } \end{cases}$		
A.	B.	B-A.	A.	B.	B-A.
487.2	487.2	0.0	487.4	487.3	-0.1
487.1	487.1	0.0	487.2	487.1	-0.1
487.2	487.0	-0.2	487.1	487.1	-0.0
487.0	487.2	0.2	487.1	487.0	-0.1
487.0	487.2	0.2	487.1	486.8	-0.3
487.1	487.2	0.1	487.2	486.8	-0.4
487.0	487.2	0.2	487.1	486.8	-0.3
487.0	487.3	0.3	487.0	486.8	-0.2
$\Delta = 0.2 \mu.$	$\Delta = 0.3 \mu.$	$\Delta = 0.5 \mu.$	$\Delta = 0.4 \mu.$	$\Delta = 0.5 \mu.$	$\Delta = 0.4 \mu.$

The first number in Column A gives the result for one place on the gauge as 487.2μ . This is the difference in readings of the two headstocks. It is not the actual length of the gauge, which for present purposes is immaterial. On moving the gauge parallel to itself, the number obtained is 487.1μ , and so on. After an interval of time, Column B is obtained and Column B-A results. Thus, consistency in the Columns A and B taken vertically shows accuracy in the gauge, and consistency when they are taken horizontally shows accuracy in the machine.

Inspection of these results shows (1) that the 2-inch single is (naturally) more consistent than the 2-inch composite, the mean values of Δ being 0.25μ and 0.45μ respectively; (2) that the inconsistencies of the machine, as shown by the B-A column, are of the same order as the irregularities of the gauges. So the apparent errors in the gauges may be attributable to the defects in the machine.

In order to see how ordinary gauges stand tests with the new machine, two 2-inch specially good standards were tested and came out as shown.

Two 2-inch Ordinary Gauges.

Gauge A.	Gauge B.
655.4	654.2
655.0	653.8
655.1	654.5
655.3	653.9
655.2	654.2
$\Delta = 0.4$	$\Delta = 0.7$

These gauges are thus less satisfactory than the Johanson gauges of the same length. But the superiority of the latter is much greater than appears, for the test was made over about three-fourths of the end faces in all cases. In the ordinary gauge this area is about 20 sq. mm., whereas in the Johanson gauge it is 350 sq. mm., or 17 times the area.

Any one who has attempted to make accurate plane surfaces in metal will allow that it is a wonderful achievement to make two planes of this size, plane and parallel to within 0.3 micron.

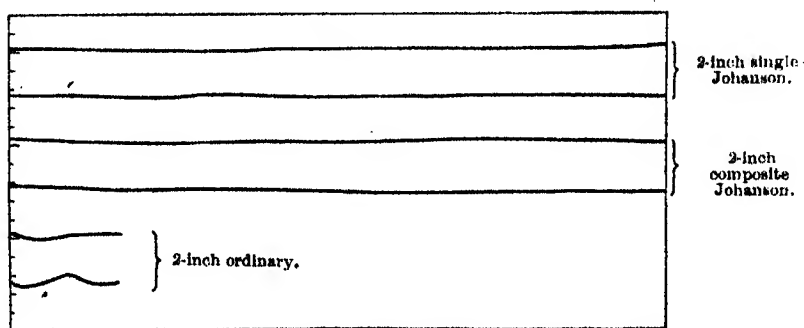


FIG. 2.

In the accompanying curves (fig. 2), the small divisions vertically represent 0.5 micron. The length of the ordinary gauge curves is about one-sixth of that of the Johanson gauges, corresponding to the diameter of the faces.

Until recently the gauge maker has insisted that the measuring machine is more accurate than the gauges it is used to measure; and that the gauges are themselves more accurate than is required for practical engineering purposes. But we here see that the best machine is powerless to detect errors in these wonderful Johanson gauges, and an advance in accuracy of the former is demanded.

The writer is now designing a machine which he hopes will give consistent readings to 0.1 micron, under the trying conditions that the gauge shall be moved parallel to itself between the readings.

In recent years the work of Michelson and of Fabry and Perot has placed the measurement of line standards of length on a high level of accuracy. An even further advance is promised by the use of Grayson's rulings by Dr. Tutton.* If a much improved measuring machine on scientific principles can be produced, the measurement of end standards should exceed in refinement that now obtaining in the parallel branch of metrology, since the latter suffers from the optical limitation of the microscope.

* See 'Phil. Trans.,' A, 1909, vol. 210.

The writer wishes to tender his thanks to Mr. J. M. C. Paton, of the firm of Manlove, Alliott, Ltd., for much assistance, freely given, in the making of gauges; also to Dr. R. T. Glazebrook, for giving him every facility in tests made on his machine at the National Physical Laboratory; also to the Royal Society for a grant which defrayed some of the cost of this work.

On the Absolute Expansion of Mercury.

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(Abstract.)

Regnault's experiments on the absolute expansion of mercury were reduced by Wüllner, and subsequently by Broch. Their reductions differed by nearly 1 per cent. at 300° C. Regnault's own reductions differed by nearly 1 per cent. from either at 40° C. Chappuis' later determinations by the weight thermometer method, which were not absolute, agreed fairly well with Wüllner's reduction of Regnault at low temperatures, but differed from Wüllner in the opposite direction to Broch by more than 2 per cent. when extrapolated to 300° C. The object of the present investigation was to repeat Regnault's method on a larger scale with modern appliances, and the apparatus was designed to secure an order of accuracy of 1 in 10,000, or 0.01° C., which, it is believed, has been substantially attained.

The principal modifications made in Regnault's apparatus were as follows:—(1) In place of the single pair of hot and cold columns, each 1.5 metres long, employed by Regnault, six pairs of hot and cold columns, each nearly 2 metres long, were connected in series as a multiple manometer, giving nearly eight times the expansion obtainable with Regnault's apparatus. (2) The difference of level to be measured was directly referred to a standard Invar scale divided in millimetres with divisions 4 microns wide, by means of a pair of telescopes with micrometer eyepieces reading to 0.001 cm. The difference of level corresponding to the fundamental interval 0° to 100° C. was 20.5 cm., so that the limit of accuracy of reading was 1 in 20,000 of this interval, or 0.005° C. The lengths of the hot and cold columns, each nearly 2 metres, could be read to 0.01 cm., giving the same order of accuracy. (3) The mean temperatures of the hot and cold

columns were observed by means of a pair of platinum thermometers equal in length to the columns, and reading to 0.002°C . The possible error of this reading would not amount to more than 0.03°C . at 300°C ., and would be much less at lower temperatures. (4) Uniformity and constancy of temperature were secured by a continuous circulation of oil, heated by means of resistance coils traversed by an electric current. The method of electric heating permitted the most delicate regulation of the temperature, even at 300°C ., with the least possible disturbance of the surrounding conditions. (5) Regnault's observations were taken with the cold column at the atmospheric temperature of 10° to 20°C ., which left the reduction to 0°C . somewhat uncertain, and was the chief cause of the discrepancy in the reduction of his observations at low temperatures. In the present investigation this uncertainty was avoided by taking a special series of observations with the cold column at 0°C . and at -10°C . (6) The chief cause of the discrepancy between the reductions of Wüllner and Broch at high temperatures appears to be that Broch applied a correction for the conduction of heat along the cross-tubes connecting the hot and cold columns in Regnault's apparatus. These cross-tubes were not quite horizontal, and introduced some uncertainty in the effective heights of the columns. In the present investigation, the cross-tubes were made of steel tube 1 mm. in bore, to diminish conduction of heat at the point where they emerged from the hot bath, and were held rigidly horizontal, by means of a specially designed bracket, for the short length in which the temperature changed from hot to cold. The effective height of the hot column was thus rendered definite and accurately measurable.

With the apparatus above described, 94 complete sets of observations were taken on 33 different days in the course of 1908, 1909, and 1910, for 16 different ranges of temperature covering the interval from -10°C . to $+300^{\circ}\text{C}$. The mean results at each temperature agree to 1 in 10,000 above 100°C ., or to 0.01°C . below 100°C ., with the following formula for the mean coefficient α from 0°C . to $t^{\circ}\text{C}$.

$$\alpha = \{1805553 + 12444(t/100) + 2539(t/100)^2\} \times 10^{-10}.$$

The results cannot be represented satisfactorily by a linear formula for the mean coefficient over the whole range; but for approximate work the following simple formula may be sufficiently exact to be of use:—

$$\alpha = (18006 + 2t) \times 10^{-8}.$$

This formula gives results which are practically correct at 100° and 200°C ., with a maximum error of 0.05°C . between 0°C . and 200°C ., but the value of the mean coefficient is more than 1 in 400 too small at 300°C .

The results of Eumorfopoulos* for the boiling-point of sulphur on the scale of the constant pressure air thermometer were about 1° C. lower than the previously accepted value 444.53° C., when reduced by the Broch-Regnault formula for the expansion of mercury; but are brought into practically perfect agreement with the old value, when reduced by reference to the results of the present investigation.

A Geometrical Proof of the Theorem of a Double Six of Straight Lines.

By H. F. BAKER, Sc.D., F.R.S.

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We assume that if two quadric surfaces have common two intersecting generators, their remaining common points lie upon a plane. This is capable of simple geometrical proof.†

Further, we prove a subsidiary theorem regarding eight straight lines, which we name 1, 2, 3, 4, 1', 2', 3', 4', which satisfy certain conditions. These conditions are first that in the scheme

$$\begin{array}{cccc} 1 & 2 & 3 & 4 \\ 1' & 2' & 3' & 4' \end{array},$$

each line intersects the three which are not in the same row or column of the scheme as itself (so that the lines can be arranged as two skew quadrilaterals, with the property that each side of either intersects a particular side of the other), and second that one of the two lines which can be drawn to meet 1', 2', 3', 4'—say a —intersects one of the two lines which can be drawn to meet 1, 2, 3, 4—say b' . The conditions for the eight lines are then briefly expressible as the existence of a scheme

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & a & \cdot \\ 1' & 2' & 3' & 4' & \cdot & b' \end{array}$$

* 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 339.

† If l and m be the common generators, intersecting in O , a variable plane α through l will touch the quadrics respectively, say, in P and P' , on l , and the ranges $\{P\}$, $\{P'\}$ will be projective with the pencil $\{\alpha\}$; these ranges have the common point O , and will thus have another common point, say A , lying on l . Similarly, let B be the point of m , other than O , at which the quadrics touch. If now H be any common point of the two quadrics not lying on l or m , the plane HAB cuts the surfaces respectively in two conics having H common and touching at A and B . These conics thus coincide in one, which constitutes the remaining curve of intersection of the quadrics.

where as before each of the ten lines of this scheme meets every line not in the same row or column of the scheme as itself. Then, denoting the point where the line $1'$ meets the plane containing the three points $(2, 3')$, $(2', 3)$, $(1, 4')$, by $(1'; 23', 2'3, 14')$, and so on, the subsidiary theorem is that the three points

$$(1'; 23', 2'3, 14'), \quad (2'; 31', 3'1, 24'), \quad (3'; 12', 1'2, 34'),$$

are collinear, and the line 4 passes through these three points.

To prove this subsidiary theorem, consider the quadric surface constructed to have the three skew lines 1, 2, a , as generators, say the quadric $(1, 2, a)$; and with it consider the quadric $(1', 2', b')$. These quadrics have common the two intersecting generators, a, b' . Their common points not lying on these common generators are therefore coplanar. Two such common points are $(1, 2')$ and $(1', 2)$. But in fact the lines $3'$ and $4'$ are generators of the quadric $(1, 2, a)$, because they meet each of the lines 1, 2, a ; and similarly the lines 3 and 4 are generators of the quadric $(1', 2', b')$. Thus, two further points of the two quadrics, not lying on the lines a or b' , are $(3, 4')$ and $(3', 4)$. Hence, the four points $(1, 2')$, $(1', 2)$, $(3, 4')$, $(3', 4)$ are coplanar. Similarly, the four points $(2, 3')$, $(2', 3)$, $(1, 4')$, $(1', 4)$ are coplanar, and so are the four points $(3, 1')$, $(3', 1)$, $(2, 4')$, $(2', 4)$. This proves that the line 4 passes through the three points

$$(1'; 23', 2'3, 14'), \quad (2'; 31', 3'1, 24'), \quad (3'; 12', 1'2, 34'),$$

which is the subsidiary theorem.

We can now proceed to the theorem of a double six of lines. This theorem is that if 11 lines be in relations expressible by the scheme

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & \\ 1' & 2' & 3' & 4' & 5' & 6' \end{array}$$

wherein each line intersects those not lying in the same row or column of the scheme as itself, then there exists a line intersecting $1', 2', 3', 4', 5'$.

(a) The given scheme includes as part of itself the scheme

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & \cdot & \\ 1' & 2' & 3' & \cdot & 5' & 6' \end{array}$$

Let the line, other than 4, which meets $1', 2', 3', 5'$ be called l , so that we have a scheme of conditions

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & \cdot & l \\ 1' & 2' & 3' & \cdot & 5' & 6' \end{array}$$

The eight lines 1, 2, 3, l , $1', 2', 3', 6'$, are thus in relations such as those considered in the subsidiary theorem. Hence the three points

$$(1'; 23', 2'3, 16'), \quad (2'; 31', 3'1, 26'), \quad (3'; 12', 1'2, 36'),$$

are collinear, and the line l may be defined as the line containing these

(b) The given scheme of 11 lines contains also as part of itself the scheme

$$\begin{array}{ccccccc} 1 & 2 & 3 & \cdot & 5 & & \\ & 1' & 2' & 3' & 4' & \cdot & 6' \end{array}$$

Let the line, other than 5, which meets $1', 2', 3', 4'$, be called m , so that we have the scheme of conditions

$$\begin{array}{ccccccc} 1 & 2 & 3 & \cdot & 5 & m & \\ & 1' & 2' & 3' & 4' & \cdot & 6' \end{array}$$

The eight lines $1, 2, 3, m, 1', 2', 3', 6'$ are therefore in relations such as those considered in the subsidiary theorem. Thus the three points

$$(1'; 23', 2'3, 16'), \quad (2'; 31', 3'1, 26'), \quad (3'; 12', 1'2, 36'),$$

all lie on the line m .

Thus l , which meets $1', 2', 3', 5'$, coincides with m , which meets $1', 2', 3', 4'$; namely, there exists a line meeting $1', 2', 3', 4', 5'$, as was to be shown.

If this line be called 6, and the line joining the points $(1, 2'), (1', 2)$, be called $[1, 2]$, we have incidentally shown that the line $[1, 2]$ meets the six lines

$$[3, 4], [3, 5], [3, 6], [4, 5], [4, 6], [5, 6].$$

If c_{12} be the line of intersection of the plane of the lines $1, 2'$ with the plane of the lines $1', 2$, the argument equally shows that c_{12} intersects $c_{34}, c_{35}, c_{36}, c_{45}, c_{46}, c_{56}$. It is only necessary to put plane for point, and point for plane throughout; in particular two quadrics with a pair of intersecting generators common, have a common enveloping quadric cone.

We have considered in the subsidiary theorem a set of eight lines satisfying conditions of the type $\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1' & 2' & 3' & 4' \end{pmatrix}$ and further subject to the unsymmetrical condition that one of the two lines which meet $1, 2, 3, 4$, intersects one of the two lines which meet $1', 2', 3', 4'$. It appears now that in such case the other line which meets $1, 2, 3, 4$, intersects the other line which meets $1', 2', 3', 4'$, and that this deduction is another form of the theorem of a double six of lines.

[Added December 12.]

Conversely consider eight lines satisfying relations typified by the scheme $\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1' & 2' & 3' & 4' \end{pmatrix}$, with the further condition that the four points $12', 1'2, 34', 3'4$, are coplanar; such a set of lines depends on 19 constants. Then it can be shown: (a) That either of the lines meeting $1, 2, 3, 4$, meets one of the lines meeting $1', 2', 3', 4'$, (b) that the points $31', 3'1, 24', 2'4$, are coplanar, (c) that the points $23', 2'3, 14', 1'4$, are coplanar, (d) that, if

$(12', 34')$ denote the line joining the points $12'$, $34'$, and so on, the four lines

$$(12', 34'), \quad (1'2, 3'4), \quad (31', 2'4), \quad (3'1, 2'4)$$

are concurrent, say, in O_1 ; the four lines

$$(12', 3'4), \quad (1'2, 34'), \quad (23', 14'), \quad (2'3, 1'4)$$

are concurrent, say, in O_2 ; and the four lines

$$(23', 1'4), \quad (2'3, 14'), \quad (31', 24'), \quad (3'1, 2'4)$$

are concurrent, say, in O_3 , (e) that if c_{12} denote the line of intersection of the planes $12'$ and $1'2$, and so on, the lines c_{23} , c_{14} , meet in O_1 , the lines c_{31} , c_{24} , meet in O_2 , and the lines c_{12} , c_{34} , meet in O_3 . The demonstrations of these results are as follows:—

(a) Draw one of the two lines which meet 1 , 2 , 3 , 4 , say, $5'$, and then draw the unique line, other than 1 , which meets $2'$, $3'$, $4'$, $5'$, calling this line 6 ; consider then the two quadric surfaces (643) and $(5'4'3')$; these will have the common intersecting generators 6 and $5'$; of the quadric $(5'4'3')$ two generators are 1 and 2 ; of the quadric (643) one generator is $2'$. As the common points of these quadrics which do not lie on $5'$ or 6 are coplanar, their plane is that determined by the points $34'$, $3'4$, $12'$; the generator 2 of $(5'4'3')$, which already meets (643) on $5'$, meets (643) in one other point lying on this plane. Now the plane of $34'$, $3'4$, $12'$, meets 2 in the point $1'2$; this point is therefore on (643) . The points $1'3$ and $1'4$ are, however, also on (643) ; hence the line $1'$ is a generator of (643) and meets 6 ; as was to be proved.

(b) The line $(13', 24')$ lies in the plane $14'$ and hence meets $(12', 34')$; it lies in the plane $3'2$, and hence meets $(43', 21')$; thus it passes through the intersection of $(12', 34')$ with $(1'2, 3'4)$. Again, the line $(31', 42')$ lies in the plane $32'$, and hence meets $(34', 12')$; it lies in the plane $1'4$, and hence meets $(21', 43')$; thus it passes also through the intersection of $(12', 34')$ with $(1'2, 3'4)$. So that the points $31'$, $3'1$, $24'$, $2'4$, are coplanar.

(c) The line $(23', 14')$ lies in the plane $24'$ and hence meets $(21', 34')$; it lies in the plane $3'1$ and hence meets $(43', 12')$; thus it passes through the intersection of $(12', 3'4)$ with $(1'2, 34')$. Again the line $(32', 41')$ lies in the plane $31'$ and hence meets $(34', 21')$, and lies in the plane $2'4$, and hence meets $(12', 43')$; thus it also passes through the intersection of $(12', 3'4)$ with $(1'2, 34')$. So that the points $23'$, $2'3$, $14'$, $1'4$ are coplanar.

(d) The line $(23', 41')$ lies in the plane $21'$ and hence meets $(24', 31')$; it lies in the plane $3'4$ and hence meets $(13', 42')$, and thus passes through the intersection of $(13', 2'4)$ with $(31', 24')$. Again the line $(2'3, 14')$ lies in the plane $2'1$ and hence meets $(2'4, 13')$; it lies in the plane $34'$ and hence

meets $(1'3, 2'4)$; thus it also passes through the intersection of $(13', 2'4)$ with $(31', 2'4')$. This establishes the existence of the points $0_1, 0_2, 0_3$.

(e) The plane $12'$, as containing the points $13', 2'4$, contains the line $(13', 2'4)$ through 0_3 ; this same plane $12'$, as containing the points $14', 2'3$, contains the line $(14', 2'3)$ through 0_3 . Again the plane $1'2$, as containing the points $1'3, 2'4$, contains the line $(1'3, 2'4')$ through 0_3 , and, as containing the points $1'4, 2'3$, contains the line $(2'3, 1'4)$ through 0_3 . The line c_{12} , in which the planes $12', 1'2$ intersect, thus passes through 0_3 . So the line c_{34} passes through 0_3 . The point 0_3 has thus a correspondence with the plane of $12', 1'2, 3'4, 3'4'$, which contains the lines $[1, 2], [3, 4]$, respectively defined as $(12', 1'2)$ and $(3'4, 3'4')$. Similarly for the points 0_1 and 0_2 .

It follows from the above that if we regard the planes of $(23', 2'3, 1'4, 1'4')$, $(31', 3'1, 2'4, 2'4')$, $(12', 1'2, 3'4, 3'4')$ as rectangular, meeting in 0 , and the plane $0_10_20_3$ as lying at infinity, the four intersections, of the pairs of the eight lines $1, 2, \dots, 3', 4'$, which lie in any one of the three rectangular planes, form a rectangle, with sides parallel to two of the axes $00_1, 00_2, 00_3$; such a rectangle is constituted for example by the points $23', 1'4, 2'3, 1'4'$, lying in 00_20_3 . It is proved above that the line $[56]$, joining the points $5'6', 5'6$, meets each of $[23], [14]$, which are the diagonals of the rectangle in the plane 00_20_3 ; thus the centres of the three rectangles lie in one straight line $[56]$. It is easy now to see that the points P_1, P_2, \dots, P_4' , in which the eight lines $1, 2, \dots, 4'$ meet the plane $0_10_20_3$ at infinity, are the projections from 0 of the corners of a rectangular parallelepiped whose edges are parallel to the rectangular axes $00_1, 00_2, 00_3$. Hence the four lines $P_1P_1', P_2P_2', P_3P_3', P_4P_4'$, are concurrent. It can be shown that their point of concurrence lies on $[56]$. Dually, if the line c_{56} , defined as the intersection of the planes $5'6', 5'6$, which is also the line of co-intersection of the three planes $(c_{12}, c_{34}), (c_{23}, c_{14}), (c_{31}, c_{24})$, be joined to the point 0 by a plane, this plane cuts the pairs of lines $(1, 1'), (2, 2'), (3, 3'), (4, 4')$, in four pairs of points, each pair being collinear with 0 .

As the tetrahedron $00_10_20_3$ gives rise to these interesting relations, I have formed the equation of the cubic surface containing the lines, and find that it may be put into the form, when x, y, z, t , are the co-ordinates referred to this tetrahedron,

$$aa'x^2(y-z-2pt) + bb'y^2(z-x-2qt) + cc'z^2(x-y-2rt) \\ - t(pyz + qzx + rxy) + t^3[(q^2-r^2)x + (r^2-p^2)y + (p^2-q^2)z] + 2pqrt^3 = 0,$$

where $a+a' = 1, b+b' = 1, c+c' = 1, p+q+r = 0$. And with this, when the co-ordinates of a line are defined by the equations $l't + mz - ny = 0, l'x + m'y + n'z = 0$, the line 4 is $\left(\frac{1}{a}, \frac{1}{b}, \frac{1}{c}, \frac{p}{bc}, \frac{q}{ca}, \frac{r}{ab}\right)$, the line 4' is obtained

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from this by replacing a, b, c , by a', b', c' , the line 1 by replacing a, b, c , by a, b', c' , the line 1' by replacing a, b, c , by a', b, c , and similarly for 2, 2', and 3, 3'. The line c_{55} is then $(1, 1, 1, 2p, 2q, 2r)$, and the line [56] is $\left(\frac{1}{aa'}, \frac{1}{bb'}, \frac{1}{cc'}, \frac{p}{2bb'cc'}, \frac{q}{2cc'aa'}, \frac{r}{2aa'bb'}\right)$. The whole figure reciprocates into itself in regard to the quadric $paax^2 + qbb'y^2 + rcc'z^2 + pqr t^2 = 0$. Of this cubic surface fifteen lines are determined rationally, namely, 1, 2, ... 3', 4', $c_{12}, c_{24}, c_{23}, c_{14}, c_{31}, c_{24}, c_{35}$, the remaining twelve, $\begin{pmatrix} 5 & 5' & c_{13} & c_{26} & c_{26} & c_{45} \\ 6 & 6' & c_{15} & c_{25} & c_{35} & c_{45} \end{pmatrix}$, which form a double six, depend upon a single square root.

OBITUARY NOTICES
OF
FELLOWS DECEASED.

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SIR BENJAMIN BAKER, K.C.M.G., K.C.B., 1840—1907.

SIR BENJAMIN BAKER was born on March 31, 1840, at Keyford, Frome, Somerset, and he died at Bowden Green, Pangbourne, Berkshire, on May 19, 1907. In a career, during the greater part of which he was associated with Sir John Fowler, K.C.M.G., he achieved the position of an engineer of the highest originality and distinction and was engaged in the design and construction of, or as responsible adviser for, a very great amount of civil engineering work of the most varied character. His connection with the Forth Bridge and the Assuan Dam alone are sufficient to mark him out as an engineer of the highest rank.

His parents were Benjamin Baker and Sarah Baker (*née* Hollis). His father appears to have come from Carlow, in Ireland, and was principal assistant at iron works at Tondy, Glamorgan. Sir Benjamin Baker was educated at the Cheltenham Grammar School. At the age of 16 he was articled to Mr. H. H. Price, of the Neath Abbey Iron Works, where some of Trevithick's pumping engines and some early locomotives and marine engines had been built. In 1860, he became assistant to Mr. W. Wilson, then in association with Mr. (afterwards Sir John) Fowler engaged in the erection of the Pimlico Railway and the Victoria Bridge and station. In 1861, he passed into the office of Mr. Fowler, where he was engaged in designing roofs, girders, and retaining walls for the Metropolitan Railway, the construction of which was then about to be commenced. He assisted in the preparation of the plans for the extension of the Metropolitan Railway and, in 1870, became Chief Assistant and junior partner to Mr. Fowler, having general charge of the construction of the Metropolitan and District Railways. His association with Sir John Fowler continued till the death of the latter in 1898.

As soon as he was engaged in Mr. Fowler's office, Baker set himself with zeal to the investigation of the mechanical problems suggested by the work on which he was engaged and the result of his studies appeared in contributions to 'Engineering,' in a series of papers on "Long Span Bridges," 1867, republished in England and America and translated and printed in Germany, Austria and Holland; "On the Strength of Beams and Columns," in 1868, also republished in 1870; "On the Strength of Brickwork," in 1872; and "On Urban Railways," in 1874.

In the articles on long span bridges, after examining the conditions for securing the greatest economy of material in the various types of girder then in use, for spans from 300 feet up to the limiting span possible, he arrived at the conclusion that, by a system of cantilevers, supporting an independent girder, an opening might be bridged which could not be spanned by any of the systems previously examined, even with an infinite amount of material. The

reasoning is throughout extremely original and instructive, and the conclusion reached was afterwards verified in the construction of the Forth Bridge. The thoroughness of the investigation was shown in the further examination of braced arch, stiffened suspension and suspended girder bridges, types as to which little experience had then been obtained. The advantage of some of these newer types in permitting erection without scaffolding is pointed out. In 1865, a project for a bridge over the Severn, with a span of 600 feet, was prepared in Mr. Fowler's office, in which it was proposed to erect successive bays by building out from each side of the main piers, carrying on the process till the two opposing halves met and formed a continuous structure. This was the system subsequently adopted at the Forth Bridge and in many bridges since.

In a revision of this treatise in 1873, a section was added on short span bridges. Baker drew attention to the fact that in short spans the action of the rolling load is the point above all others requiring attention. His experience had forced on him the conviction that the destructive action of a frequently recurring load, not small compared with the dead load, was at that time habitually underrated. This was one of the earliest recognitions in this country by a practical engineer of the law of fatigue which Wöhler had discovered.

It may also be mentioned in this connection that Baker, in 1887, contributed to the 'Transactions of the American Society of Mechanical Engineers' "Some Notes on the Working Stress of Iron and Steel." He pointed out that while in some bridges in which the ratio of dead to live load was large, stresses of 17,000 to 20,000 lbs. per sq. inch had proved to be safe, yet in small spans such stresses would quickly lead to destruction. Hence in the elevated railway of New York the stresses were limited to 8000 lbs. per sq. inch in the flanges and to 4500 in members subject to reversals of stress. He gave the results of a series of experiments similar to those of Wöhler on soft and hard steel and iron. These showed that the opinion of some engineers, that alternating stresses are destructive only if they exceed the elastic limit, is erroneous. He indicated that the resistance of riveted joints to slipping is due to frictional adherence and stated that in the Forth Bridge the stress on riveted joints was kept within the limit of adherence. He expressed further the opinion that both the old-fashioned Government regulations requiring a fixed working stress for all kinds of loading and modern formulæ based on Wöhler's results failed to meet the requirements of engineers.

In a further series of articles in 'Engineering,' in 1868, "On the Strength of Beams, Columns, and Arches," republished in 1870, Baker discussed a problem which troubled many engineers at that time, namely, that the ultimate strength of beams is widely different from the strength calculated on the assumption that the material is elastic up to rupture. He adopted as an explanation Barlow's theory, which would not now be accepted, the discrepancy being known to be due to plasticity. But Baker used a mass of practical data and derived his coefficients so that his results were approxi-

mately true and useful. He applied his investigation to the then important question of the relative strength and stiffness of different sections of rails.

Like all Baker's papers, these articles contained many experimental observations carefully and accurately made.

The first great work on which Baker was engaged in a position of responsibility was the construction of the London Underground Railways, and his connection with this work continued till the completion, in 1871, of the sections from Moorgate Street to the Mansion House, a length of 13 miles. He described the works, which were of a specially novel, difficult, and expensive character, in a paper in the '*Proc. Inst. Civil Engineers*,' vol. 81, 1884—85, and discussed generally the problem of Urban Railways in some important papers in '*Engineering*' in 1874. He pointed out in these articles that at the time of the inception of the system of underground urban railways, none of the engineers concerned, either as promoters or opponents, evinced the dimmest intuition of the fact that the traffic over an urban line might be the heaviest in the world, and of a character to test the capabilities of a locomotive engine to the uttermost. It was even proposed at first to work the trains with locomotives carrying a charge of hot water, and an engine of this type was built, with unsatisfactory results. It was this intention which led to an insufficient provision for ventilation, which afterwards gave much trouble. In portions of the line constructed later, the stations were in open cutting, and a length of open cutting was introduced between the stations. Baker pointed out the great expenditure of power in acceleration required with stations half a mile apart and suggested that an ideal urban railway should undulate, the stations being placed at the summit of the undulations. By this means gravity would assist the engine in starting and supplement the brakes in stopping. He was able to carry out this arrangement subsequently in the construction of the Central London Tube Railway. He indicated the necessity for great tractive force to ensure a reasonable mean speed and the need of powerful brakes, because the time occupied in accelerating and reducing speed is a large fraction of the whole time of transit when the stations are not far apart. He showed that the laws governing urban traffic were widely different from those obtaining on ordinary railways, and that with weak engines and inefficient brakes the horse-power would vary as the cube of the speed. He calculated that with a level line and moderate speed about 60 per cent. of the energy of the engine is expended in the mischievous work of grinding the brake blocks, and that of 36 lbs. of fuel used per train mile only 15 lbs. would be usefully employed. He checked his calculations by observations on the Metropolitan Railway, where, with the powerful engines used, the mean speed was only 12 miles an hour. He showed that with an undulating railway with the stations at the summits, 50 per cent. more speed could be obtained with the same fuel consumption as on the existing railway.

The building of shallow underground railways through the heart of a great city involved a host of new and unexpected problems in construction and

difficulties in dealing with the pipes, sewers, and other obstructions below the street surface, and in supporting, with as little damage as possible, the heavy buildings above the railway.

Baker was largely concerned in the introduction of electrically worked tube railways in London. He was Consulting Engineer to the South London, the first tube railway, and the still more important Central London Railway was constructed under his superintendence. This railway, of $6\frac{1}{2}$ miles in length, consists of two tunnels of circular section, built with a casing of cast-iron segments, 11 feet 6 inches in diameter. At the stations the cylinders are 21 feet 6 inches in diameter. The railway is generally about 60 feet below the street level, and few difficulties or obstructions were met with. In this railway the stations are at the summit of undulations, the gradients falling each way so that the arrangement suggested in the early papers on urban railways was for the first time carried out. The railway was commenced in 1896 and opened by the late King, then Prince of Wales, in 1900.

From the year 1869, Mr. Fowler was much engaged in Egypt in advising the Khedive Ismail Pasha in regard to various engineering projects for developing the resources of the country, and Baker made more than one visit to Egypt to assist his partner, and later became Consulting Engineer to the Egyptian Government. One result of studies then undertaken was the project for the Soudan Railway between Wady Halfa and Shendy near Khartoum and a ship incline at Assuan. By means of a railway 3 kiloms. in length, over which boats, floated in a cradle, could be dragged by hydraulic machinery of 400 h.p., the obstacle to navigation at the first cataract was to be overcome, and continuous navigation without change of boat established between Wady Halfa and Lower Egypt. From Wady Halfa a railway of 550 miles length and of 3 feet 6 inches gauge was to be constructed at a cost of £4,000,000, to tap the rich southern provinces; about 60 miles were constructed and then the financial difficulties of Egypt compelled the interruption of the work.

Another great project in Egypt in which Fowler and Baker were concerned, in 1875, was a Ship and Irrigation Canal (an alternative Suez Canal) *viâ* Cairo and Alexandria. The project embraced a sweet water ship canal, 118 miles in length, from Alexandria to Cairo, and another from Cairo to Suez, a distance of 122 miles. At Cairo, low water is 39 feet above sea level, so that there would be a current down the canals to the Mediterranean and Red Sea. The rate of the current would be manageable and would depend on the amount of water abstracted for irrigation. Locks were to be provided on both stretches of the canal. For crossing the Nile at Cairo a railway bridge was to be provided, connecting the lines on the two sides of the river, and serving to support a traversing mooring to which ships could be attached when crossing the river. It was estimated that the payments for irrigation water would give a handsome return on the expenditure, independent of ship dues. In 1883, when the question of doubling the Suez Canal was mooted, Baker and Fowler, in an article in the 'Nineteenth Century Magazine,' recalled attention

to the advantages of this project, not only as providing an alternative ship canal, but as a means of affording high level irrigation and reclaiming a large area of desert.

Sir B. Baker was, at various times, consulted about the repairs and additions to the Delta Barrage, erected originally by French engineers, which had proved incapable of sustaining the required head of water in consequence of the unsatisfactory foundation. After various partial repairs by Sir Colin Scott Moncrieff, Sir W. Willcocks, and Colonel J. H. Western, it has finally been rendered completely stable and satisfactory by Major Sir Hanbury Brown.

A result of Baker's visits to Egypt was a paper on the hydrology of the Nile,* dealing with the slope, variation of level and flow, and amount of solids carried, largely based on his own observations.

In 1875, Garibaldi, then at the zenith of his popularity, was urging the Italian Government to undertake the diversion of the Tiber, in order to prevent the flooding of Rome and the Campagna. The Government considered the cost of the project prohibitive, but it had to be treated seriously. Baker and Fowler were called into counsel. Some surveys were made, and finally more moderate plans of rectification and embankment were adopted.

In 1878, Baker designed a vessel to bring Cleopatra's Needle to this country. Messrs. John and Waynman Dixon first suggested the removal of the obelisk, Mr. Fowler and Lord Vivian obtained the Khedive's consent, and Mr. Erasmus Wilson offered a contribution of £10,000 for the purpose. While in the case of the Luxor Obelisk, at Paris, the removal occupied seven years, Cleopatra's Needle was erected on the Embankment 18 months after the order to build the vessel was given. Baker designed a vessel of circular section, in which the needle was rolled into the water and towed to Alexandria. There final arrangements were made, and thence the vessel was towed to England. Unfortunately, in a storm, some rails used as ballast broke loose, and the crew in a panic abandoned the vessel. This accident was due to an oversight, but the vessel was never in real danger. She was found, towed to Ferrol, and then to England. The Needle was fitted with trunnions, lifted in a horizontal position, and then swung to a vertical position, the operation being carried out with the greatest ease.

Following some earlier abortive proposals, the Forth Bridge Company was formed in 1873, to erect a suspension bridge with spans of 1600 feet, designed by Sir T. Bouch. But the failure of the first Tay Bridge, also designed by Sir T. Bouch, led to reconsideration of the plans, the suspension principle was abandoned, and a design for a steel cantilever and central girder bridge, with spans of 1710 feet, submitted by Messrs. Fowler and Baker, was adopted. The construction of this great bridge involved the co-operation of many distinguished engineers and contractors, and its successful completion is an achievement in the honour of which they all share. But, no doubt, the

* 'Proc. Inst. Civil Engineers,' vol. 80, 1879—80.

general design is due to Baker, who carried out for the first time the provisions of his early treatise on long span bridges. Sir John Fowler and Sir B. Baker also kept a personal and continuous control over the entire operation of building the bridge. The contract was let in December, 1882, and the opening ceremony took place, under the auspices of the Prince of Wales, on March 4, 1890. This is not the place to enter upon a description of this immense work. Baker gave an account of the bridge in a paper at the British Association in 1882, and at the meeting at Montreal in 1884; also in his Presidential Address at the Mechanical Section of the British Association in 1885, and in papers at the Iron and Steel Institute in 1885, and at the Royal Institution in 1887. Reference may also be made to the admirable record on the Forth Bridge reprinted from 'Engineering' in 1890, and to "Die Forth Brücke," von G. Barkhausen, 1889. An exceedingly important and troublesome question in designing the Forth Bridge was the provision to be made for wind pressure. The failure of the first Tay Bridge was due, at any rate to a great extent, to the lateral pressure of the wind, and subsequently, perhaps, excessive values had been assumed for the intensity of wind pressure. In the case of the Forth Bridge, the immense area exposed made the question of wind pressure a governing consideration in design. The maximum wind pressure in accordance with the Board of Trade rule was assumed as 56 lb. per square foot, acting on twice the vertical projection of one side of the bridge. But to remove doubts as to the adequacy of this provision, experiments were made. A wind gauge of 300 square feet area was erected on the island of Inchgarvie, with small comparison gauges. Some account of these experiments was given in the Montreal paper on the Forth Bridge, and in the 'Proc. Inst. Civil Engineers,' vol. 69, p. 145, and vol. 156, p. 119. They satisfied Baker that the assumed pressure was in excess of anything likely to be realised. Further experiments were made on the shielding effect of one surface on another surface behind it. A suspended cross bar carried an adjustable flat surface at one end and a model of any structure of more complex form at the other. By oscillating this simple apparatus and adjusting the plane surface, the plane area equivalent in resistance to the more complex model was found. The results were very interesting and valuable.

Baker had had great experience in the use of steel, and had made very many experiments on its behaviour under straining action. His confidence in it was great, and in designing the Forth Bridge he ventured to use, for the compression members, steel of higher tenacity than had previously been adopted in structures. He thus anticipated the tendency to use high tensile steel, which is now not uncommon in suitable cases.

In 1881, Sir Benjamin Baker contributed a paper to the 'Proceedings of the Institution of Civil Engineers,' on the "Lateral Pressure of Earthwork." He pointed out the deficiency of experimental investigation, and criticised adversely the theories of earth pressure on which engineers chiefly relied. The paper contains a mass of instructive observations on the pressure of

earth and the failures of retaining walls. The paper gave rise to a very interesting discussion, and to a communication from the veteran mathematician, Boussinesq. A very characteristic statement from Baker's reply to the discussion may be quoted:—"He protested against the charge implied against him of a contempt for theory. His habit of thought and mode of working were entirely opposed to such a feeling, and indeed, in his opinion, an engineer who did not attempt to classify his practical data, with the ultimate aim of elucidating a satisfactory theory, was wilfully playing the part of a blind man." Another important practical paper, based on a very large experience, was one on "Railway Springs."*

Egypt is a country nearly rainless, and dependent on the Nile for its water supply. Hence, irrigation from the river has been practised from a great antiquity. But the water supply is insufficient in the summer months for perennial irrigation in middle and lower Egypt, and the level of the river is too low to adequately feed the canals. The satisfactory repair of the Delta Barrage made the question of increasing the flow at low Nile a very urgent one. In 1889, Colonel J. W. Western, R.E., began an investigation of projects for storing water in the winter months to increase the river flow in summer. On his retirement, Sir W. Willcocks, who was appointed Director of Reservoirs, continued the study and prepared three schemes, one for a reservoir in the Wady Rayyan, two for reservoirs in the Nile Valley, near the First Cataract. Generally, the scheme for a reservoir near Assuan was favoured, the reservoir being formed by constructing a masonry dam across the river. It was shown that if such a scheme were carried out, not only could the supply of the existing irrigation canals be ensured at all times, but a large increased area of land could be brought into profitable cultivation. In flood, the River Nile carries so much silt that water then impounded would gradually but certainly fill up a reservoir with deposit. It was necessary, therefore, that a dam should be so constructed as to allow the silt-bearing flood water to pass through, and to impound water only when the river flowed clear. Sir W. Garstin, Secretary to the Public Works Department, generally endorsed the views of Sir W. Willcocks. At his suggestion, an International Commission of distinguished engineers was then appointed by Lord Cromer to report on the plans, consisting of Sir B. Baker (England), Mr. Giacomo Torricelli (Italy), and M. Auguste Boulé (France). The two former reported adversely to the other plans, but favourably to the scheme of a reservoir at Assuan, suggested some modifications of the designs of Mr. Willcocks, and selected a site for the dam. M. Boulé reported separately, dissenting from the views of his colleagues, not on the ground of any doubt as to the practicability of the scheme proposed from an engineering point of view, but from an objection to any interference with the temples at Philæ, which, on the scheme recommended, would be partially submerged. As to the absolute need of a reservoir, no doubt was expressed

* 'Proc. Inst. Civil Engineers,' vol. 66.

by any member of the Commission. It was estimated that its construction would increase the revenue of the State by £750,000 annually, and would result in benefit to cultivators of ten times that amount. Baker suggested that, as a last alternative, the temples at Philæ could, if necessary, be raised 40 feet at an expenditure of £200,000.

In the plans of Sir W. Willcocks, the height of the dam was to be 85 feet, and the reservoir capacity 88,300 million cubic feet. To meet objection to the submersion of Philæ, the height of the dam was reduced to 65 feet, and the reservoir capacity to 37,612 million cubic feet.

In 1898, Sir Ernest Cassel entered into financial arrangements with the Government, taking bonds repayable in 30 years, and engaging to supply the funds necessary during the progress of the undertaking. A contract was signed with Messrs. John Aird and Company, and Sir B. Baker was appointed Consulting Engineer. The dam consists of two parts, one 4600 feet in length, pierced by 180 sluices at four levels, the other 1800 feet long and solid. A lock and canal makes the passage of the cataract easy to steamers at all times, thus making the Nile continuously navigable up to the Second Cataract at Wady Halfa. The work was carried out successfully, and completed in 1902, in less than the contract time. The Assuan Reservoir extends to Ibrim, a distance of 140 miles from the dam.

On the plan carried out, the water-level, with reservoir full, rose to the floor of the Philæ temples, then situated on an island in the reservoir. It was found that parts of the foundations of these temples were on silt and in a bad state, and likely to be further damaged by the action of the water. Underpinning with steel girders surrounded with cement on an extensive scale was carried out with considerable difficulty and at great cost, and the stability of the masonry of the temples was secured.

A subsidiary work was simultaneously executed at Asyût, 339 miles below Assuan and 246 miles above Cairo. From this point a large area is irrigated by the Ibrahimia Canal, which was with difficulty supplied during the summer months. By the construction of a dam across the Nile a permanent supply could be ensured, and with the larger flow in the river due to the Assuan Reservoir, a considerably increased area in Middle Egypt could be placed under perennial irrigation. The original plans were prepared by Sir W. Willcocks, Sir B. Baker was appointed Consulting Engineer, and the work was carried out by Messrs. Aird. The river is 2953 feet in width, and the dam is an arched viaduct, founded on a masonry floor, with sluices in the openings. The urgent importance of an early completion of the work being realised by Sir B. Baker, he advised that the contract should be cancelled, the work pushed on regardless of cost, and the question of profit to the contractors left to himself. Lord Cromer and the contractors agreed to these terms, the work was finished a year under the contract time, and the Public Works Department admitted that £600,000 had been saved to the country owing to the extra year's supply of water.

In 1902, Sir Benjamin Baker gave a lecture on the Nile dams at the Royal Institution, at which the Prince and Princess of Wales were present. He contributed an article on the "Nile Reservoirs and Philæ" to the 'Nineteenth Century' magazine in 1894. (Reference may also be made to papers by Mr. Maurice Fitzmaurice, C.M.G., "On the Nile Reservoir, Assuan," 'Proc. Inst. Civil Engineers,' vol. 152, p. 71; by Mr. F. W. S. Stokes, "On the Sluices and Lock Gates of the Nile Reservoir, Assuan"; and by G. H. Stephens, C.M.G., "On the Barrage at Asyût," 'Proc. Inst. Civil Engineers,' vol. 158, p. 26.)

The success of an immense work of this kind must depend on the energy, the ability, and the resourcefulness of a great number of persons, and, in speaking of it at the Institution of Civil Engineers, Sir B. Baker gave unstinted praise to his colleagues in Egypt who carried out the operations in a trying climate. But undoubtedly the reliance placed by Lord Cromer and those in authority on Sir Benjamin Baker's experience and judgment was an important factor in undertaking the work; he spent time every winter on the works; he provided beforehand, by careful foresight and consideration, for difficulties which might arise, and his wise direction, resourcefulness, and courage were essential elements in the success achieved.

The construction of the Assuan Reservoir proved of immediate and enormous advantage to the prosperity of Egypt, and it very soon became evident that a still larger supply of irrigation water was necessary. By 1905, the whole of the water stored at Assuan was appropriated, though a vast area of land was still left without water, and the increase in the value and productivity of the irrigated land exceeded expectations.

A site for a second reservoir above Assuan was sought, but no suitable position could be found. Finally, it was decided to raise the dam at Assuan 7 metres, or about to the height at first contemplated by Sir W. Willcocks. It is a matter of regret that this will involve the partial submergence of the Philæ temples during part of the year. But it can at least be said that this was not decided on till every alternative had been examined and unavoidably rejected. The addition of new to old masonry in a work which has to resist water pressure, and in a country where the temperature changes are great, is a matter of considerable difficulty. Sir Benjamin Baker considered long and anxiously the method of proceeding, and under his direction some very interesting experiments were carried out on model dams to elucidate the distribution of stress. Ultimately he developed a plan for strengthening and raising the dam by constructing an independent mass of masonry free to settle and contract, after which it will be bonded to the older mass by cement grouting.

Shortly before his death he went to Egypt, and there the plans were decided on and the contract settled. Before long, the dam will be increased in height so that the storage capacity of the reservoir will be increased two and a-half times.

It is not needful in this notice to enumerate Sir Benjamin Baker's

professional works, but amongst the more important the following may be mentioned: He was, with Sir John Fowler, Chief Engineer for the remarkable Chignecto Ship Railway, which was commenced, but the works were stopped by the failure of the contractor, and finally abandoned by the Canadian Government. Jointly with Sir John Wolfe Barry, he was Consulting Engineer for the Avonmouth Docks; Engineer for the electrically-operated bascule bridges over the Swale on the South Eastern Railway and at Walney at Barrow-in-Furness; Consulting Engineer to the Public Works Department of Cape Colony, and responsible for the bridges erected there; Consulting Engineer, jointly with Mr. Shelford, for the West African Railways. He was called into council when the boring of the Hudson River Tunnel at New York seemed likely to be a failure, and designed a special form of shield by means of which the work was carried on. Jointly with Dr. Deacon he reported on the schemes for the supply of water to London from Wales.

Sir Benjamin Baker was a member of the Light Railways Commission of the Board of Trade; and of a Committee which reported to the Board of Trade in 1900, on the loss of strength in steel rails due to prolonged use, a Committee appointed after the serious accident at St. Neots due to a fractured rail. He was a member of the Standards Committee, instituted at the suggestion of the Institution of Civil Engineers, a Committee which is engaged on the large and important work of establishing standard forms, tests and specifications for all the materials used by engineers and standard types for locomotives and electrical machinery. In 1888, he was appointed a member of the Ordnance Committee at Woolwich and was senior civil member at the time of his death. This Committee, consisting of military, naval, and civil members, decides on all questions as to design, material, etc., of the war material manufactured in the Arsenal and small arms factories of the Government, and to his duties on it Baker gave unremitting attention.

He was member of a Committee appointed to consider the interference with the work of Greenwich Observatory due to the London County Council generating station on the bank of the river immediately below the Observatory. He was a member of the Executive Committee of the National Physical Observatory.

Sir B. Baker was often called in to advise as to the safety of structures which, erected at an earlier period, exhibited signs of decay, and to suggest means of reparation. Thus he reported on the condition of three of Telford's principal bridges, the Buildwas cast-iron arch bridge, the Over masonry arch bridge over the Severn near Gloucester, and the Menai suspension bridge. He succeeded in restraining the local authorities from pulling down two of these or doing anything which would affect their appearance. In the case of the Menai Bridge, he reported that the main chains were sound and that though the suspending rods had suffered from corrosion they would last till the present timber floor required renewal. When this became necessary he recommended the substitution of a steel floor and the repair of the suspending rods. He reported to the Dean and Chapter on the stability of St. Paul's

Cathedral. When part of the roof of Charing Cross Station fell, he made an immediate examination at some risk and on his advice the whole roof was reconstructed and the similar roof at Cannon Street Station strengthened.

Sir Benjamin Baker was the recipient of many distinctions and took an active part in many scientific societies. At the opening of the Forth Bridge he received the decoration of K.C.M.G., and for services at Assuan the K.C.B. and the order of Medjidieh of the First Class. He received the honorary degree of D.Sc. at Cambridge, that of LL.D. at Edinburgh, and that of M.Eng. at Dublin. The French Academy of Sciences awarded to him and to Sir John Fowler the Poncelet prize. He became Fellow of the Royal Society in 1890, member of its Council in 1892—3, and was one of its Vice-Presidents from 1906 till his death. At the Institution of Civil Engineers he became an associate in 1867, member in 1877, member of Council in 1882, and was President in 1895. He became member of the Institution of Mechanical Engineers in 1890, of its Council in 1899. He was on the Council of the Society of Arts from 1888 and took an active part in its affairs, also member of the Iron and Steel Institute, and hon. A.R.I.B.A. and A.I.N.A. He was made an honorary member of the American Society of Civil Engineers in 1897, of the American Society of Mechanical Engineers in 1886, and of the Canadian Society of Civil Engineers in 1888.

Sir Benjamin Baker was always very modest in speaking of his own part in undertakings for which he was responsible, and very generous in acknowledgment of the help he received from colleagues. He was always very ready to discuss with others the difficulties which arose from time to time, and he treated opinions put before him with much consideration, though always forming an independent judgment. He was actively generous in helping younger engineers, and for those who served him he long retained his goodwill, and often continued to correspond with them for years. He attended very closely to the business of numerous councils of which he was a member, and his judgment on the matters which arose was rapid, tolerant, and sagacious, and always carried great weight.

W. C. U.

EDWARD JOHN ROUTH,* 1831—1907.

By the death of Dr. Routh on June 7, after a period of gradually failing health, a commanding figure in the recent history of English mathematics has been removed. Born at Quebec in 1831, the son of a distinguished British officer, he was educated in London at University College School, and subsequently studied mathematics under de Morgan at University College. He matriculated at Peterhouse in 1850, but did not drop his London connection, obtaining the gold medal in mathematics with the degree of Master of Arts in 1853, then a somewhat rare distinction. At Peterhouse he had Clerk Maxwell, who soon after migrated to Trinity, as his rival in the same year; while Tait and Steele were undergraduates of the College, and Lord Kelvin (already Prof. W. Thomson, of Glasgow) was a junior Fellow.

Not long after taking his degree—in January, 1854, being Senior Wrangler, and bracketed with Clerk Maxwell for the Smith's prizes—he began the career of tuition of advanced honour men in mathematics, which was soon to lead to a unique reputation as a successful teacher. From 1858 to 1888 he had, in all, between 600 and 650 pupils, of whom the great majority graduated as Wranglers, twenty-seven being Seniors, while forty-one were Smith's prizemen; between 1861 and 1885, when he retired from this strenuous work at the age of 54, he had all the Senior Wranglers as pupils, with but one exception near the end of the time.† The number of his pupils, which was for many years about 100, was not at all unprecedented; what was unique was the fact that for all this time he directed, almost without challenge, most of the intellectual activity of the *élite* of the undergraduate mathematical side of the University. This herculean task naturally demanded methodical arrangements, and the husbanding of his resources to the utmost. What he aimed at was to impart thorough mastery of the main principles of ascertained knowledge over the field of mathematics then cultivated at Cambridge; it was clearly out of the question to stray very far into the regions of nascent science, in which ordered theory gradually evolves itself in response to concentrated and specialised effort. He was in the habit of claiming that this would follow spontaneously in the case of the mathematician born, once he had learnt mastery of the resources of the science, while even when it did not follow, the record in the legal and other professions of persons who had done well in youth in mathematical studies proved their supreme value as a deductive mental discipline.

His plan was to take small classes, each of about ten men selected to run together, and to maintain an average by catechetical methods. Those

* Reprinted from 'Nature,' June 27, 1907.

† These and other facts have been taken from a valuable notice in the 'Cambridge Review,' signed W. W. R. B.

who could go faster than the average had extra material provided in the form of manuscript digests for study, and especially in the institution of a weekly paper of about a dozen problems, selected from recent examination papers, or abstracted from memoirs in the home and foreign mathematical journals. An element of competition formed a stimulus in answering these papers, while written solutions were afterwards at hand for study in cases of failure to unravel them. Looking back on those times, it might be thought that there was too much problem and too little sustained theory; but no one ever accused the standard of the problems selected of being lower than it ought to be, while, on the other hand, absence of some such rigid procedure would have rendered quite impossible that focussing of undergraduate mathematical activity and ambition in one place, which was a main feature of the system. Men with further ambitions would struggle with Thomson and Tait's "Natural Philosophy" or with Maxwell's "Electricity," or with brilliant and stimulating courses of lectures given on growing special subjects by the more eminent mathematical physicists, and thus learn that though in youth mastery may be rapid, yet at all times invention must be slow. It was, moreover, thus possible for the abler men to have time to spare, to expand their outlook by taking up some other branch of knowledge as a relaxation from mathematics, or for joining in other activities of the University. Nowadays the field covered by the mathematical instruction offered at Cambridge is vastly wider than would have been conceived as practicable twenty years ago; but the question is still unsettled how far it is expedient to extend the preliminary undergraduate course into complex special theories.

Whatever may be thought as regards Dr. Routh's views on postponing special research in favour of thorough preparation, it could not be urged that he did not himself, notwithstanding his other absorbing work, set an example of what research might be. Many of his earlier papers, mainly in the 'Quarterly Journal of Mathematics,' related to the dynamics of rigid solids, spinning tops, rolling globes, precession and nutation, and such like; they were distinguished by the development of methods relating to moving systems of co-ordinate axes, and to the differentiation of vectors such as velocity and momentum with regard to them. In another connection he applied the kinematics of special systems of co-ordinate axes, moving along a curve, to problems of curvature and torsion. The advantages of these methods in differential geometry have come again into recognition, as may be seen in such works as Darboux's "Théorie des Surfaces." Afterwards, arising out of his researches on dynamical stability, which will be referred to presently in more detail, there came a series of papers in the 'Proceedings of the London Mathematical Society,' on the propagation of waves, and the analysis of complex vibrations in networks of interlacing threads, and in other such laminar systems, leading up to a mechanical treatment or illustration of the broad general theory of harmonic analysis, principal periods, and related topics.

In the early 'seventies, the question of the possible explanation of steady, including apparently statical, relations of material systems by the existence of latent steady motions, such as the rotations of concealed fly-wheels or gyrostats attached to the system, was much to the fore. The fundamental problem as regards such representations is their degree of permanence; for a state of motion which falls away, however slowly, cannot be appealed to in elucidation of secular steadiness of relations. At a later stage the ideas of the subject were crystallised by Lord Kelvin in his British Association address, Montreal, 1884, entitled "Steps towards a Kinetic Theory of Matter," and in later addresses on cognate topics, mainly reprinted in vol. i. (Constitution of Matter) of his "Popular Lectures and Addresses," culminating in a way in 1897 in his gyrostatic model of a rotationally elastic optical æther.

It is thus not surprising that the Adams prize subject at Cambridge for the period 1875-7, announced over the signatures of Challis, Clerk Maxwell, and Stokes, should have been the search for "The Criterion of Dynamical Stability." This subject suited Routh's predilections exactly; and his classical essay, "A Treatise on the Stability of a Given State of Motion, particularly Steady Motion," composed, as he states in the preface, almost entirely during the year 1876, was the result. The greater part of the work in the essay is analytical, and is concerned with the discussion of the nature of the roots of the algebraic equation determining the free periods of slight vibration of the dynamical system; but where it enters upon the discussion of dynamical principles, such as the criteria connected with the Energy and the Action, the essay moves in a high plane. In particular, the burning question of how adequately to represent latent, and therefore unknown, steady motions, such as those of concealed fly-wheels or gyrostats attached to the system, is solved at a stroke by the famous theorem of the "modified Lagrangian function." It was established, in fact, that the presence of concealed steady motions does not fundamentally alter the standard mode of analytical specification of dynamical interaction developed originally by Lagrange, except in the one respect that the effective Lagrangian function now involves terms linear in the velocity-components as well as quadratic terms. The procedure of Lagrange, evolved originally from the side of the Principle of Action, constituted the science of general dynamics by eliminating from the problem all variables the values of which are prescribed in terms of the remaining ones by relations of permanent constraint, thus reducing the dynamical analysis to the discussion of just as many quantities as are required to specify the state of the system. It gives cause for some surprise that nearly a century elapsed before the correlative step was taken, namely, the elimination, from the analytical specification of the system, of permanently steady or cyclic motions, as well as the permanent geometrical constraints above mentioned. In the hands of the analysts who treated the subject meanwhile, the requirements of the actual planetary and lunar theories were perhaps the main aim; it is only recently, and largely

in the hands of the English school, notably Lord Kelvin and Clerk Maxwell, in later conjunction with Helmholtz, and building largely on the earlier work of W. Rowan Hamilton, that the subject of general dynamics has been welded into an instrument for the inductive, and in many cases speculative, exploration of physical processes in general. Anyhow, it will be evident how fundamental an advance in the principles of the dynamical interpretation of nature was involved in Routh's formulation of what he called the "modified Lagrangian function."

The problem thus solved by Routh with remarkable simplicity had already been some time in evidence. In the first edition of Thomson and Tait's "Natural Philosophy" in 1868, the equations of Lagrange had been applied in most effective manner to problems of motions of solids in fluid media, the energy function involved being determined in terms of the motions of the solids alone, and the fluid thus being *ignored* in the subsequent work. This procedure was soon challenged by Kirchhoff, as going beyond the existing conditions of validity of general dynamical theory; a special justification for the case of motion in fluids was given by him, on the basis of a Least Action analysis, and a brief statement of it was included by the author in the German translation of the treatise. Soon afterwards the same difficulty was pressed on Lord Kelvin independently by J. Purser, who also published a justification on more physical lines. This was, not unlikely, the origin of Lord Kelvin's general theory of "ignorance of co-ordinates," first published in 1879 in the second edition of Thomson and Tait's treatise, but which probably existed in manuscript anterior to Routh's essay. A report was once current that most of it was worked out in the harbour of Cherbourg, while his yacht was refitting, and the carpenters were all the time hammering overhead. This form of the theory, though more expressly suggested by the needs of physical dynamics, was less complete in one respect than Routh's, in that it did not bring the matter into direct relation with a single characteristic function (Lagrangian function of Routh, kinetic potential of Helmholtz), but simply obtained and illustrated the equations of motion that arose from the elimination of the cyclic co-ordinates that could be thus ignored.

Later still, Helmholtz, in his studies on monocyclic and polycyclic kinetic systems, which began in 1884, and culminated in the important memoir on the physical meaning of the Principle of Least Action in vol. c. (1886) of 'Crelle's Journal,' developed the same theory more in Routh's manner, and built round it an extensive discussion of physical phenomena, so that on the Continent the whole subject is usually coupled with his name. Shortly before, the work of Routh and Kelvin had already been co-ordinated with the Principle of Action by more than one writer in England.

The most elaborate published result of Dr. Routh's scientific activity was the "Treatise on the Dynamics of a System of Rigid Bodies," which began as a thorough, though rather difficult, handbook in one octavo volume, but expanded in successive editions in a manner of which other classical instances

readily occur to mind, until it became a sort of cyclopædia of the dynamical section of theoretical physics. In the course of an inquiry some ten years ago as to the reason why English mathematical physicists had so much practical command over the application of their knowledge, the mode of teaching in Cambridge came under review; and in particular this book was discovered by Prof. F. Klein, of Göttingen, who made arrangements for its introduction to the Continental public in a German translation, containing some brief valuable annotations such as the wide analytical outlook at Göttingen suggested. Especially was emphasis given to the great extension of the scope of abstract dynamics above described, with which Routh's name was associated, it is to be hoped permanently. Somehow the book does not seem to have attracted even yet much sustained attention in France.

Until lately, Dr. Routh's presence was a familiar and welcome one to residents in Cambridge. Though he never sought public positions, his services were in requisition in many ways, as Senator and Fellow of the University of London, as member of the University Council at Cambridge, member of Council of the Royal Society, and in other activities; while he declined more prominent offices more than once. In society he was bright and attractive, though somewhat retiring, simple, and entirely free from any suggestion of superiority. The respect and affection which he inspired in a long succession of distinguished pupils found expression on the occasion of his partial withdrawal from work in 1888, when at a remarkable gathering of judges, engineers, and men of science, his portrait by Herkomer was presented to Mrs. Routh, with many expressions of warm appreciation. His leisure he employed mainly in mathematical research, and in the preparation of a series of treatises on subjects of mathematical physics, of which the only criticism to be made is that his wealth of valuable material tended to convert them into cyclopædias rather than text-books. His last public action was to take the lead in opposition to the proposals for change in the system of the Mathematical Tripos at Cambridge. It is possible that he did not fully realise the altered circumstances of the time, and the insistent claims of other studies; anyhow, it will be matter for congratulation if the new arrangements work as well and as smoothly as did the older Mathematical Tripos during the long period when the practical direction was mainly in his hands.

J. L.

DMITRI IVANOVITCH MENDELÉEFF, 1834—1907.

THE name of Mendeléeff has long been honoured by the Royal Society. Though not the first to recognise a relation between the properties of the elements and their atomic weights, he was unquestionably the first to apply the principles embodied in the statement of the "Periodic Law" to the settlement of atomic weights, to the prevision of previously unknown elements, and to the recognition of the true relations of different groups of elements to one another. In recognition of the importance of these generalisations and of the great knowledge and enthusiasm with which he laboured at the subject, the Royal Society awarded to him, in 1882, the Davy Medal, jointly with Prof. Lothar Meyer, in 1892 the Fellowship of the Society, and in 1905 the Copley Medal.

Dmitri Ivanovitch was the fourteenth child of his father, Ivan Pavlovitch Mendeléeff, Director of the Gymnasium at Tobolsk, in Siberia. His mother, Marie Dimitrievna, belonged to the old Russian family of Kornileff, long settled as manufacturers of paper and glass in the neighbourhood of Tobolsk, the glass works being situated at the village of Aremziansk. There can be no doubt that Dmitri Ivanovitch owed much of his intellectual activity to his mother, who was evidently a woman of considerable mental power and self-instructed beyond the range of ordinary female education of that period. This debt Mendeléeff acknowledges in the introduction to his great work on Solutions, which he dedicated to the memory of his mother in the following interesting lines: "This investigation is dedicated to the memory of a mother by her youngest offspring. She could only educate him by her own work, conducting a factory. She taught by example, corrected with love, and to devote him to science she left Siberia, spending her last resources and strength. When dying she said, 'Refrain from illusions, insist on work and not on words, search patiently divine and scientific truth.' She knew how often dialectical methods deceive, how much there is still to be learned, but how with the aid of science, without violence, with love but firmness, all superstition, untruth and error are removed, bringing in their stead the safety of discovered truth, freedom for further development, general welfare, and inward happiness. D. Mendeléeff regards as sacred a mother's dying words. October, 1887." How full of energy she was is shown by the fact that at her husband's death she continued to manage the glass works at Aremziansk.

At the age of fifteen, Dmitri Ivanovitch came from his far-off birthplace to Moscow in order to continue his education. A year later he entered the chief Pedagogic Institute in St. Petersburg, where, being associated with the University, he was able to devote himself chiefly to the physical sciences. At the end of this course he was appointed teacher in the Government school at Simferopol in the Crimea, and later at the gymnasium at Odessa.

In 1856 he returned to St. Petersburg, and at the early age of twenty-two he was appointed "privat-docent" at the University. At this time, like most young chemists, to judge by the titles of his published papers, he passed rapidly from one subject to another, but he soon found matter for serious thought and experiment in the physical properties of liquids, especially in their expansibility by heat.

In 1859, by permission of the Minister of Public Instruction, Mendeléeff proceeded to Heidelberg, where, in a private laboratory, he devoted himself to further study of the physical constants of chemical compounds, communicating some of his results to 'Liebig's Annalen' and to the French Academy. Returning to St. Petersburg in 1861 he secured his doctorate, and was appointed soon afterwards Professor of Chemistry in the Technological Institute. In 1866 he became Professor of General Chemistry in the University, Boutleroff at the same time holding the Chair of Organic Chemistry. He was frequently employed by the Government in connection with the investigation of questions of technical importance, and notably concerning the oil supplies of Baku and the Caspian; also in the department of weights and measures. The latter service brought him on several occasions to England, where his remarkable and distinguished figure was quite familiar in scientific circles. In 1904 he celebrated his seventieth birthday, on which occasion he received congratulatory addresses from the Chemical Society of London, and from many other scientific associations and academies with which he was connected.

Mendeléeff died on February 2 (N.S.), 1907, followed three days later by his colleague Menshutkin.

The chief scientific work of Mendeléeff may be roughly classified under several heads. As already mentioned, some of his earliest labours related to the determination of physical constants, especially the dilatation of liquids, which resulted later in the establishment of a simple general formula for the expansion of liquids between 0° and their boiling points. Later, he was led to discuss that theory of solutions which regards them as consisting of definite chemical compounds of the solvent with the solute, existing in a liquid state and more or less completely dissociated. This theory he supported by his own experiments, especially on mixtures of sulphuric acid and water and of alcohol and water. The densities of the latter have been estimated with very great accuracy, and from them he isolated two out of three assumed compounds represented by the formulæ (1) $C_2H_6O + 12H_2O$, (2) $C_2H_6O + 3H_2O$, and (3) $3C_2H_6O + H_2O$. In this connection it is interesting to recall the fact that Mendeléeff was a declared opponent of the doctrine of free ions in solutions of electrolytes.

A third subject to which he gave much attention was the nature and the sources of petroleum. After visiting the Caucasus, he went in 1876 to see the oil fields of Pennsylvania, and on his return communicated to the Russian Chemical Society a theory concerning the formation of hydrocarbons in the earth's crust. Rejecting the hypothesis that these compounds resulted

from the decomposition of organic remains, he assumed, on various grounds, that the interior of the earth must consist largely of metals, iron predominating. Such a view, in consideration of the relatively high mean density of the earth, was already familiar; but supposing metals such as iron and manganese saturated with carbon, Mendeléeff explained the production of hydrocarbons from these compounds by contact with water at a high temperature. The resultant hydrocarbons would distil from the lower into the more superficial layers of the earth's crust, leaving oxides of the metals behind.

The subject with which especially the name of Mendeléeff is indissolubly connected is the development of the Periodic Law. The several stages in the history of the recognition of relations between atomic weights and properties of elements extend over more than half a century. So soon as a sufficient number of atomic weights had been estimated with some approach to accuracy, by Berzelius and others, the hypothesis of Prout attracted attention, and down to the time of Stas was regarded with some favour. In 1829, Doebereiner pointed out the existence of triads of closely related elements, such as chlorine, bromine, iodine—lithium, sodium, potassium, in which the atomic weights are so related that the middle term of each series is nearly the arithmetical mean of the two extremes. Thirty years later Dumas drew attention to the close analogy observable in such series with homologous series of carbon compounds.

The first step toward the recognition of a periodic relation was taken in 1864—5 by John Newlands, and this was followed, soon afterwards, by a scheme of the known elements, arranged by Odling. But Newlands' attempt was very imperfect, as many of the elements were incorrectly placed, and no room was left for discovery of new elements. Odling, at the end of his article, refers to the probable existence of "some hitherto unrecognised general law."

The question being left in this condition, Mendeléeff communicated to the Russian Chemical Society, in March, 1869, a paper on "The Relations of the Properties to the Atomic Weights of the Elements." An abstract published in the '*Zeitschrift für Chemie*' (vol. 5, p. 405) contains several obvious misprints; but, correcting these, the following literal translation serves to show that Mendeléeff had discovered this unrecognised law and perceived most of its important consequences:—

"When the elements are arranged in vertical columns according to increasing atomic weight, so that the horizontal lines contain analogous elements again according to increasing atomic weight, an arrangement results from which several general conclusions may be drawn. (Here follows the table of elements.)

"1. The elements, arranged according to magnitude of atomic weight, show a periodic change of properties.

"2. Chemically analogous elements have atomic weights, either in close agreement (Pt, Ir, Os), or increasing by equal amounts (K, Rb, Cs).

"3. The arrangement according to atomic weights corresponds with the *valency* of the elements and, to a certain extent, to the difference in chemical behaviour, *e.g.*, Li, Be, B, C, N, O, F.

"4. The elements most widely distributed in nature have small atomic weights, and all such elements are distinguished by their characteristic behaviour. They are thus typical, and the lightest element, hydrogen, is therefore rightly chosen as the typical unit of mass.

"5. The magnitude of the atomic weight determines the properties of the element, whence, in the study of compounds, regard is to be paid not only to the number and properties of the elements and their mutual action, but to the atomic weights of the elements. Hence the compounds of S and Te, Cl and I, show, beside many analogies, striking differences.

"6. The discovery of many *new* elements may be foreseen; for example, analogues of Si and Al, with atomic weights between 65 and 75.

"7. Some atomic weights will presumably suffer correction; for example, Te cannot have the atomic weight 128, but 123 to 126.

"8. From the table, new analogies become apparent. Thus, U appears as an analogue of Bo and Al, which is in harmony with experience."

Many years later, Mendeléeff found a difficulty in placing the elements of the argon group and radium, these substances having been discovered long subsequently to the formulation of the "periodic" scheme.

In an article written for the 'Russian Encyclopædia,' and abstracted into English ('Nature,' November, 1904), he later acknowledges the independent existence of these elements, and places the argon group in a column by themselves. The first place in the same column is assigned to the ether, which he assumed to be molecular in structure with a very small atomic weight.

How some of his earlier predictions have been verified by the discovery of gallium, of scandium, and of germanium, which correspond to Mendeléeff's theoretical elements, ekaluminium, ekaboron, and ekasilicon, is matter of common knowledge, and supplies a complete justification of the scheme. And though there are some outstanding difficulties about individual elements, the construction of this scheme and the enunciation of the periodic law as a principle applicable to the whole of the chemical elements constitute one of the most fertile conceptions in the whole range of modern chemistry.

W. A. T.

GEORGE GORE, 1826—1908.

GEORGE GORE was born in 1826 at Bristol, where his father had a small business as a cooper. Leaving school at thirteen, he began work as an errand boy. At seventeen he was apprenticed to a cooper and worked at that trade till he was twenty-one, meanwhile studying science and making what experiments he could in his small leisure. He was from the first keenly interested in electro-deposition, and probably it was through his desire to pursue this subject that in 1851 he came to Birmingham, already the chief centre of electroplate manufacture, and here he spent the rest of his life. He appears to have supported himself at first by practising medical galvanism, the apparatus for which he had already improved while at Bristol. Meanwhile he held classes on electroplating and on chemistry and thus began his long career as a teacher in Birmingham. Later he was appointed Science Master at King Edward's School, a post which he held for many years.

In 1854 he published the first of a series of papers on the electro-deposition of metals and soon gained a reputation which led manufacturers in Birmingham and elsewhere to bring their difficulties to him for solution, and from this time onwards he held a leading position in the town as a consulting chemist. Perhaps his most important work consisted in the help which he gave in the early days to the art of electroplating by his numerous discoveries, many of them the basis of present day practice. He wrote several text-books on the subject, which have been widely used here and abroad.

For a time he was chemist to a phosphorus works, and while in that position he discovered the method of bleaching phosphorus by chlorine, which is still in use.

His best known contribution to pure science is his investigation of the properties of anhydrous hydrofluoric acid, which he succeeded in preparing chemically pure. This work occupied him for several years, from 1860 onwards, and was followed by a research on the properties of silver fluoride. Among other researches were investigations on properties of liquid carbonic acid, on ammonia as a solvent of the alkaline metals, and on the thermo-electric action of metals and liquids.

An indefatigable and incessant experimenter, he made many minor discoveries. In 1854 he found that antimony deposited under certain conditions in which it contained a small quantity of antimony trichloride was an unstable form, so that when struck or rubbed or touched with a red hot wire it suddenly rose in temperature to over 300° C. and changed from a black lustrous body to a greyish powder. This form he termed "Explosive Antimony."

In 1858 he invented "Gore's Sphere," an interesting modification of the Trevelyan Bar experiment, in which a sphere is set rolling round a pair of

circular heated rails and continues to roll round. He further found that the sphere would roll round the rails without other heat than that supplied by an electric current passed from rail to rail through the sphere.

Another discovery was that if a current is passed through a solution of mercuric cyanide and caustic potash between two pools of mercury, a series of crispations appear on the negative pool and humming sounds are given out.

A more important discovery, made in 1868, was that there is a critical point in iron as it cools from a red heat. He found that as a red hot wire begins to cool it suddenly lengthens and then contracts again. He showed that there was no converse effect on raising the temperature, and that the effect on cooling was accompanied by a change in magnetic permeability.

Dr. Gore was an ardent advocate for the endowment of research, writing in its support at a time when its importance was not recognised as it is to-day. Among his publications is a volume on "the Scientific Bases of National Progress," in which he urged the value of scientific research to the welfare of the nation. His views were to some extent realised in the foundation, about 1880, of an "Institute of Scientific Research" by a few citizens of Birmingham. Here Dr. Gore was installed and here he worked for the remainder of his life.

Besides a volume on "the Art of Scientific Discovery," Dr. Gore occupied his later years, when he was no longer able to experiment so vigorously, in the composition of two works on "the Scientific Basis of Morality" and on "the New Scientific System of Morality." In these he treated of morals from a materialistic point of view, for which he might have found more sympathy fifty years earlier.

Dr. Gore was elected a Fellow of the Royal Society in 1865, and in 1877 he received the degree of LL.D. from the University of Edinburgh. In 1891 he was given a Civil List Pension in recognition of his contributions to science. He died on December 20, 1908, when nearly eighty-three years of age.

By his will his residuary estate was equally divided between the Royal Society and the Royal Institution for the purpose of assisting original scientific discovery. The share of the Royal Society, amounting to nearly £2,500, has been invested as "the Gore Fund."

J. H. P.

JULIUS THOMSEN, 1826—1909.

HANS PETER JÜRGEN JULIUS THOMSEN, distinguished for his thermochemical investigations, was born in Copenhagen on February 16, 1826. He was educated at the church school of St. Peter in that city, and subsequently at the von Westens Institute. In 1843 he commenced his studies at the Polytechnic, and in 1846 graduated there in Applied Science, and became an assistant to Prof. E. A. Scharling. Of his earliest years comparatively little is known. Thomsen, always a reserved and taciturn man, talked little about himself even to his intimate friends—and least of all about the days of his youth. It was known to a few that these days had not been smooth. Those who were best informed were conscious that to these early struggles much of that dour and resolute nature which formed a distinguishing trait in his character was due.

In 1847 he became assistant to Forchhammer, and for a time supplemented his scanty income by teaching agricultural chemistry at the Polytechnic. In 1853 he obtained a travelling scholarship, and spent a year in visiting German and French laboratories. He probably owed this scholarship in great measure to his first contribution to the literature of chemistry, namely, his memoir, 'Bidrag til en Thermochemisk System' (contributions to a thermochemical system), communicated to the Royal Society of Sciences of Copenhagen in 1852, for which he received the silver medal of the Society and a sum of ten guineas to enable him to procure a more accurate apparatus. In this memoir he sought to develop the chemical side of the mechanical theory of heat, doubtless under the influence of Ludwig Augustus Colding, an engineer in the service of the Municipality of Copenhagen, and a pioneer, like Mayer, in the development of that theory. Indeed, the Danes now claim for Colding, who had made experiments on the relation between work and heat as far back as 1842, but whose labours were practically ignored by his contemporaries, the position which the Germans assign to Mayer (see Mach's 'Development of the Theory of Heat'; also Tait's 'Sketch of Thermodynamics,' 1868, § 33). In 1861 Thomsen further developed his ideas in a memoir on the "General Nature of Chemical Processes, and on a Theory of Affinity based thereon," published in the 'Transactions of the Danish Academy of Sciences.' In this paper he laid the foundations of the chief scientific work of his life.

In 1853 Thomsen patented a method of obtaining soda from cryolite, so-called "Greenland," or ice-spar, a naturally occurring fluoride of sodium and aluminium, $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$, found largely, indeed, almost exclusively, in Greenland, and particularly at Ivigtut. In 1854 he obtained the exclusive right of mining for cryolite and of working up the mineral in Denmark for soda and alumina. Actual manufacturing operations were begun on a small scale in 1857, and in the following year Thomsen planned the present large

factory at Oeresund, near Copenhagen, which was opened on his thirty-fourth birthday. The importance of this industry to Denmark may be seen from the circumstance that during the fifty years of its existence the firm have paid the Danish Government nearly £300,000 for the concession. From the start Thomsen took a large share in the management of the Oeresund works, and by his energy, foresight, and skill placed the undertaking on a sound commercial basis.

Although Thomsen died a rich man, mainly as the result of the industry he created, in the outset of his career as a teacher and a technologist his means were very straitened. He came of poor parents, of no social position or influence, and they were unable to further his inclinations towards an academical career. In 1854 he applied unsuccessfully for a position as teacher of chemistry at the Military High School in Copenhagen. During three years—from 1856 to 1859—while still engaged in developing his cryolite process, he acted as an adjuster of weights and measures to the Municipality of Copenhagen. It was a poorly paid position, but it kept the wolf from the door. At about this period he betook himself to literature, and published a popular book on general subjects connected with physics and chemistry—somewhat in the style of Helmholtz's well-known lectures—entitled '*Travels in Scientific Regions*,' which had a considerable measure of success. He was, however, not altogether unknown even at this time as an author, since in 1853 he had collaborated with his friend Colding in producing a memoir on the causes of the spread of cholera and on the methods of prevention, which attracted much attention at the time of its appearance.

In 1859, whilst engaged in the Oeresund factory, he again applied to the authorities for a position as teacher at the Military High School, and succeeded in obtaining an appointment to a lectureship in physics, which he held until 1866. During his tenure of this office he devised his polarisation battery, which received many awards at International Exhibitions and was used for a time in the Danish telegraph service.

In 1859–60 he was "vicarius" for Scharling at the University, and in 1865 became a teacher, and in the following year Professor of Chemistry and Director of the Chemical Laboratory, a position which he retained—active to the last—until 1901, when he retired in the seventy-fifth year of his age.

Before his connection with the University, he founded and edited, from 1862 to 1878, in association with his brother, August Thomsen, '*the Journal of Chemistry and Physics*,' one of the principal organs of scientific literature in Denmark.

In 1863 he was elected a member of the Commission of Weights and Measures, and was instrumental in bringing about the adoption of the metric system and the assimilation of the Danish system to that of the Scandinavian Kingdom.

In 1883 Thomsen became Chancellor of the Polytechnic High School of Copenhagen—a position which he held for about nine years. During this period he entirely changed the character and spirit of the school, and stamped

it with the impress of his earnestness and industry. Under his direction, new buildings were erected and arranged in accordance with the best Continental and American models.

It was while occupying the position of Director of the Chemical Laboratory of the University that Thomsen executed the thermochemical investigations which constitute the experimental development of the ideas he had formulated in his memoir of 1861. The results of these inquiries were first made known in a series of papers published from 1869 to 1873 in the 'Transactions of the Royal Danish Society of Sciences,' and from 1873 onwards by the 'Journal für Praktische Chemie.' The papers were republished in collected form in four volumes (1882-1886) by a Leipzig house under the title of 'Thermochemische Untersuchungen.' A summary of this experimental labour, which extended over a third of a century, was subsequently prepared by Thomsen, and published in 1905 in Danish under the title of 'Thermokemiske Resultater.' A translation of this volume by Miss Katharine A. Burke, entitled 'Thermochemistry,' renders it readily accessible to English readers.

To go through this material in detail is impossible here. It may be stated generally that practically every simple inorganic process has been investigated calorimetrically by Thomsen, or can be calculated by means of the calorimetric data furnished by him. In the case of organic substances, data have been given for estimating the heat of combustion of a large number of compounds. All these estimations were made by Thomsen personally, according to a pre-arranged plan, and in systematic succession during a period of more than thirty years. They comprise more than 3500 calorimetric estimations. It has been truly said that this work is unique in the chemical history of any country.

Among the results of Thomsen's thermochemical inquiries which have special value for physical chemistry is his investigation of the phenomena of neutralisation, in which he shows that the basicity of acids can be estimated thermochemically, and that it can in this way be proved whether or not a point of neutrality exists. His observation that the heat of neutralisation is the same for a long series of inorganic acids, such as hydrochloric acid, hydrobromic acid, hydriodic acid, chloric acid, nitric acid, etc., supports the theory of electrical ionisation, inasmuch as this requires that the heat of neutralisation of the strong acids must in all cases be independent of the nature of the acid, because the process of neutralisation for all of them is the combination of the ion of hydrogen in the acid with the ion of hydroxyl of the base to form water. These investigations also led to the important thermochemical result that the heat of neutralisation of acids (or the heat of their dissociation) cannot be considered as a measure of the strength of the acids.

Another important result is the proof by experiment of the connection which exists between the gradient of the heat-effect with the temperature and the specific heat of the reacting substances. The law of conservation of energy

requires the relation $dU/dT = C_1 - C_2$, where U is the heat-effect, T the temperature, and C_1 and C_2 are the heat capacities of the two systems before and after the reaction; and Thomsen showed by investigation of the heat of neutralisation, the heat of solution, and the heat of dilution, that this relation was satisfied, thus verifying the precision of his determinations. For the purpose of his inquiry, the specific heats of a large number of solutions of salts were estimated by an ingenious method, and with an exactness hitherto unattained.

Of no less importance are Thomsen's thermochemical investigations on the influence of concentration on chemical equilibrium. In the year 1867 Guldberg and Waage published their molecular theory of the chemical effect of mass. But they had only verified the theory to a small extent and in particularly simple cases. They had not investigated the complete homogeneous equilibrium, because at that time no method existed for its experimental investigation. Thomsen showed that the estimation could be made thermochemically. By allowing, for instance, an acid to act on a salt of another acid in an aqueous solution, the latter acid will be partly replaced by the first, which will form a salt. By mixing, for instance, a solution of sodium sulphate and nitric acid, there are formed sodium nitrate and sulphuric acid, but the process will not proceed to completion. If we have estimated the heat of neutralisation of the two acids with sodium hydroxide, the difference between these two heat-phenomena will give the amount of heat corresponding to the total decomposition of the sodium sulphate, and the heat found experimentally by mixing the two solutions will therefore show to what degree the transformation has taken place. It would be possible to estimate thermochemically the amount of the four substances in solution, and thereby, by varying the concentration or the proportion between the initial quantities of substances, to calculate whether the Guldberg-Waage theory on the effect of mass was confirmed in this case.

Thomsen applied this method to a large number of different acids and bases, and was thus enabled to prove agreement with the law of the influence of mass in all the cases which he examined. He found particularly that the proportion of the one acid which remained combined with the base was constant with mixtures of constant proportion. On this basis he propounded the term *avidity* for the tendency of the acid to unite with the base, and he verified that the avidity was independent of the concentration, and only to a small extent varied with the temperature. The idea of avidity has since acquired great utility, particularly since other and more exact methods for its estimation have been found. Concurrently with this, its meaning has been made clear by the theory of ionisation.

On the basis of these estimations, Thomsen drew up the first table, based on experiments, of the relative strength of the acids, and the numbers in this table have been found to agree with the results obtained by examining the electrical conductivity of the acids.

It is worth noting that Thomsen not only produced the experimental proof

of the correctness of the Guldberg-Waage theory of the effect of concentration soon after the appearance of this theory, but also that he was the first to acknowledge and adopt it. It is remarkable that this work of Thomsen received so little attention, although it appeared in a widely circulated German journal, and it was not until ten years later that the law of the effect of mass was generally recognised, as the result of the work of Ostwald and van't Hoff.

Although Thomsen's title to scientific fame rests mainly upon his thermochemical work, his interests extended beyond this particular department of physical chemistry. He worked on chloral hydrate, on selenic acid, on ammoniacal platinum compounds, and on glucinum platinum chloride, on iodic acid and periodic acid, on hydrogen peroxide, hypophosphorous acid, and hydrogenium. He early recognised the importance of Mendeléeff's great generalisation, and contributed to the abundant literature it produced. His paper of 1895, "On the Probability of the Existence of a Group of Inactive Elements," may be said to have foreshadowed the discovery of the congeners of argon. He pointed out that in a periodic function the change from negative to positive value, or the reverse, can only take place by a passage through zero or through infinity; in the first case, the change is gradual, and in the second case it is sudden. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with a passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element which is electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132, the first five numbers corresponding fairly closely with the atomic weights respectively of helium, neon, argon, krypton, and xenon ('*Zeitsch. anorg. Chem.*,' 1895, vol. 9, p. 283; '*Journ. Chem. Soc.*,' 1896, vol. 70, II, p. 16). He subsequently made known the existence of helium in the red fluorite from Ivigtut.

As evidence of Thomsen's manipulative ability and his power of accurate work may be mentioned his determination of the atomic weights of oxygen and hydrogen, and incidentally of aluminium. For the atomic weight of hydrogen he obtained the value 1.00825 when $O = 16$, which is practically identical with that of Morley and Noyes. He further made most accurate estimations of the relative densities of these gases, and of the volumetric ratios in which they enter into the composition of water. His value for the atomic weight of aluminium is nearly identical with that adopted in the last Report of the International Committee on Atomic Weights.

Thomsen maintained his interest in thermochemical problems up to the end, and was a keen and clear-sighted critic of the work which appeared from time to time during the later years of his life. This interest

occasionally gave rise to controversy, and some of his latest papers were wholly polemical.

Thomsen was a pronounced atomist, and to him a chemical process was a change in the internal structure of a molecule, and the chief aim of chemistry was to investigate the laws which control the union of atoms and molecules during the chemical process. He considered that chemistry should be treated mathematically as a branch of rational mechanics. But no one insisted more strongly than he how little we really know of these questions. In summarising his theoretical ideas in the '*Thermokemische Resultater*,' he says, "An almost impenetrable darkness hides from us the inner structure of molecules and the true nature of atoms. We know only the relative number of atoms within the molecule, their mass, and the existence of certain groups of atoms or radicals in the molecule, but with regard to the forces acting within the molecules and causing their formation or destruction, our knowledge is still exceedingly limited." He fully realised that his own work was only the foundation on which the future elucidation of these questions must rest. "He worked," says Brönsted, "in the conviction that what we somewhat vaguely call the affinity of the atoms—their interaction, their attraction, its varying effect, etc.—follows the general dynamical laws, and that, as he worded it, the principle that 'might is right' holds good in chemistry as in mechanics. On this foundation he hoped it might be possible to evolve the laws for the statics and dynamics of chemical phenomena, even although the inner nature of the action is unknown."

Thomsen's merits as an investigator received formal recognition from nearly every country in the civilised world. As far back as 1860 he was elected one of the thirty-five members of the Danish Royal Society of Sciences of Copenhagen, and from 1888 until his death he was its President. In 1876 he became an Honorary Foreign Member of the Chemical Society of London. On the occasion of the fourth centenary of the foundation of the University of Upsala (created in 1477) he received the degree of Doctor of Philosophy *honoris causa*. In 1879 he was made an honorary M.D. of the University of Copenhagen. Two years later he was made a Foreign Member of the Physiographical Society of Lund, and in 1888 he was elected a member of the Society of Science and Literature of Gothenburg. In 1885 he became a member of the Royal Society of Sciences of Upsala, and in 1886 of the Stockholm Academy of Sciences.

In 1883 he and Berthelot were together awarded the Davy Medal of the Royal Society—a fitting and impartial recognition on the part of the Society of the manner in which the two investigators, whose work not infrequently brought them into active opposition, had jointly and severally contributed to lay the foundations of thermochemistry.

In the same year Thomsen was made a member of the Accademia dei Lincei of Rome, and in the following year he was elected into the American Academy of Arts and Sciences in Boston, and of the Royal Academy of Sciences of Turin. In 1887 he was made a member of the Royal Belgian Academy.

In 1886-87, and again in 1891-92, he was Rector of the University of Copenhagen. In 1888 he became Commander of the Dannebrog, and in 1896, and on his seventieth birthday, he was made Grand Commander of the same order. On the same occasion the Danish chemists caused a gold medal to be struck in his honour. In 1902 he became a Privy Councillor (*Geheime Konferenz raad*). In the same year he was elected a Foreign Member of the Royal Society of London.

He died on February 13, 1908, and was buried on the eighty-third anniversary of his birth and on the jubilee of the opening of the Oeresund factory. His wife, Elmine Hansen—the daughter of a farmer on Langeland—predeceased him in 1890.

Thomsen played many parts in the intellectual, industrial, and social development of Denmark. To Europe in general he was mainly known as a distinguished man of science. By his fellow citizens he was further recognised as an educationist of high ideals, actuated by a strong common sense and a stern devotion to duty; as an able and sagacious administrator; as a successful technologist and the creator of an important and lucrative industry based upon his own discoveries; and as a man of forceful character, who brought his authority, skill, and knowledge of men and affairs to the service of the communal life of Copenhagen.

Thomsen was a municipal councillor of that city for more than a third of a century. He occupied a commanding position on the Council, and was invariably listened to with respect. The gas, water, and sewage works of Copenhagen are among the monuments to his civic activity. From 1882 up to the time of his death he was a member of the Harbour Board of the port. In these respects Thomsen sought to realise Priestley's ideal of the perfect man—that he should be a good citizen first and a man of science afterwards.

T. E. T.

WILLIAM JAMES RUSSELL, 1830—1909.

WILLIAM JAMES RUSSELL was born on May 20, 1830, the son of a banker at Gloucester. His grandfather, William Russell, lived at Birmingham and was an intimate friend of Priestley. He suffered for this friendship by having his house burned to the ground by the Birmingham mob, in the Church and King Riots of 1791, two days after Priestley's house had met the same fate.

Young Russell, the subject of this notice, was educated at private schools, at Bristol and Birmingham, and entered University College, London, in 1847, where he studied chemistry under Thomas Graham (afterwards Master of the Mint) and Alexander Williamson. In 1851 he was appointed the first demonstrator of chemistry at the then newly-founded Owens College, and assisted Professor (afterwards Sir Edward) Frankland to plan and superintend the building of the original chemical laboratories of the College. In those days, every man who wished to train himself seriously as a chemist spent some time at a foreign University, mostly in Germany. Accordingly, after remaining at Manchester for two years, Russell went to Heidelberg, where he worked under Bunsen from the autumn of 1853 to that of 1855 and took his degree, Ph.D. After returning to England, he lectured for some time at the Midland Institute, Birmingham, but went back to University College, London, in 1857, as assistant to his former teacher, Williamson. At this time the methods of gas-analysis were receiving much attention from chemists in consequence of the precision given to them by Bunsen. This precision, however, was attainable only by the application of numerous corrections involving comparatively laborious calculations. It occurred to Williamson that these corrections might, in nearly all cases, be dispensed with if the pressure and temperature of the gas to be measured were made the same as those of a fixed quantity of air caused to occupy always the same volume. Under these conditions it is not necessary, for comparative measurements, to observe the actual temperature and pressure of the gas: the quantity of it is directly proportional to its volume without further correction. Russell joined Williamson in devising apparatus by means of which this idea could be applied practically with accuracy and convenience, and he continued to occupy himself in improving the details for several years.

Among the results of Russell's purely chemical work, we may mention his discovery of the precipitation of silver from an aqueous solution of silver nitrate by gaseous hydrogen, and the determination of the atomic weights of cobalt and nickel. By decomposing the oxides with hydrogen he obtained, in 1863, the values $\text{Co} = 29.370$ and $\text{Ni} = 29.369$, and six years later, by measuring the hydrogen evolved when the metals are dissolved in hydrochloric acid, he obtained $\text{Co} = 29.88$ and $\text{Ni} = 29.35$. The corresponding numbers given by the International Table of Atomic Weights for 1908 are $\text{Co} = 29.5$

and Ni = 29.35 (the actual numbers of the International Table are here halved to make them comparable with Russell's units).

Dr. Russell was among the earliest investigators of the absorption spectra of what are commonly counted colourless liquids. He and Mr. Lapraik, who assisted him in experiments on this subject, remark: "We have been able to find but few liquids which in columns of 6 or 8 feet do not give absorption spectra." As examples of his acuteness in following up casual observations and his ingenuity and perseverance in varying their conditions, we may mention his experiments "On the action of certain metals and other bodies on a photographic plate in the dark" and "On the formation of definite figures by the deposition of dust." He traced the effects dealt with in the former of these investigations almost certainly to the formation of traces of peroxide of hydrogen. Those described in the latter paper were successfully explained by Mr. J. Aitken, F.R.S., who devised an ingenious method of observing the actual process of formation of the figures.

Russell was long engaged in teaching work. From 1860 to 1870 he was Professor of Natural Philosophy at Bedford College (London). From 1868 to 1870 he was lecturer on chemistry in the Medical School of St. Mary's Hospital and from 1870 to 1897 he held a similar appointment at St. Bartholomew's Hospital. Both here and at St. Mary's he succeeded the late Dr. Augustus Matthiessen, F.R.S. He was elected a Fellow of the Chemical Society in 1851; he became Secretary of the Society in 1873, Treasurer in 1875, retaining the office for fourteen years till, in 1889, he was elected President. During his presidency, in 1891, the Society celebrated the fiftieth anniversary of its foundation. He was an original member of the Institute of Chemistry, founded in 1877, and was President from 1894 to 1897.

Russell was for twenty-five years, 1878 to 1903, a member of the Council of Bedford College (London) and Chairman from 1887, and his attention and sound judgment contributed greatly to the prosperity of the College.

He was elected Fellow of the Royal Society in 1872; he served twice on the Council and was a Vice-President from 1897 to 1899. He presided over the Chemical Section of the British Association at the meeting at Bradford in 1873.

Personally, Dr. Russell was quiet but genial in manner, and he was very highly valued by a large circle of friends. He married, in 1862, a daughter of the late A. Follett Osler, F.R.S., of Edgbaston. He died, November 12, 1909, at his house at Ringwood, leaving one son and one daughter.

In the preparation of this notice, use has, by permission, been made of an article published in 'Nature,' vol. 82, p. 101 (Nov. 25, 1909).

G. C. F.

SIMON NEWCOMB, 1835—1909.

SIMON NEWCOMB was born in Nova Scotia in 1835, at Wallace, a pretty village at the mouth of the river of that name. His father was a country school teacher, a nomadic profession in a thinly-populated district. He was the most rational and most dispassionate of men. Newcomb in his autobiography (which will be freely quoted in this notice) tells us that his father had learned from careful study "that the age at which a man should marry was twenty-five. A healthy and well-endowed offspring should be one of the main objects in view in entering the marriage state, and this required a mentally-gifted wife. She must be of different temperament from his own, and an economical housekeeper. So when he found the age of twenty-five approaching he began to look about. There was no one in Wallace who satisfied the requirements.

"He therefore set out afoot to discover his ideal. In those days and regions the professional tramp and mendicant were unknown, and every farmhouse dispensed its hospitality with an Arcadian simplicity little known in our times. Wherever he stopped overnight he made a critical investigation of the housekeeping, perhaps rising before the family for this purpose. He searched in vain until his road carried him out of the province. One young woman spoiled any possible chance she might have had by lack of economy in making the bread. She was asked what she did with an unnecessarily large remnant of dough which she left sticking to the sides of the pan. She replied that she fed it to the horses. Her case received no further consideration.

"The search had extended nearly a hundred miles when, early one evening, he reached what was then the small village of Moncton. He was attracted by the strains of music from a church, went into it, and found a religious meeting in progress. His eye was at once arrested by the face and head of a young woman playing on a melodeon, who was leading the singing. He sat in such a position that he could carefully scan her face and movements. As he continued this study, the conviction grew upon him that here was the object of his search. That such should have occurred before there was any opportunity to inspect the dough-pan may lead the reader to conclusions of his own. He inquired her name—Emily Prince. He cultivated her acquaintance, paid his addresses, and was accepted." "My mother was the most profoundly and sincerely religious woman with whom I was ever intimately acquainted, and my father always entertained and expressed the highest admiration for her mental gifts, to which he attributed whatever talents his children might have possessed. The unfitness of her environment to her constitution is the saddest memory of my childhood. More I do not trust myself to say to the public, nor will the reader expect more of me."

His early years were passed amid social conditions of the utmost simplicity.

"The women sheared the sheep and made the clothes, but any man who allowed wife or daughter to engage in heavy work outside the house would have lost caste."

As a child, Newcomb was precocious in arithmetic, doing extraordinary calculations for his years with the assistance of a napped counterpane.

He was never known to deviate from the truth in one single instance either in infancy or youth. This high praise comes from his father, who adds a little later: "You were uncommonly deficient in that sort of courage necessary to perform bodily labour. Until nine or ten years of age you made a most pitiful attempt at any sort of bodily or, rather, handy work."

He was an omnivorous reader, and a very careful one, never passing a word that he did not understand.

Among his neighbours he acquired a reputation for learning that he felt was not appreciated, while he was painfully conscious of his inability to drive oxen. And he says: "My boyhood was, on the whole, one of sadness." At the age of sixteen Newcomb almost decided upon the trade of a carpenter, but at the last moment he was apprenticed for five years to a certain Doctor Foshay, who turned out to be a quack. While he was with the doctor: "A book peddler going his rounds offered a collection of miscellaneous books at auction. I bought, among others, a Latin and a Greek grammar, and assiduously commenced their study. With the first I was as successful as could be expected under the circumstances, but failed with the Greek, owing to the unfamiliarity of the alphabet, which seemed to be an obstacle to memory of the words and forms."

At the end of two years he ran away and worked his passage on board ship to Salem.

The year 1854 was spent as teacher in a country school. In 1855 he got a better position of the same character at Sudlersville.

The next year he taught in the family of a planter named Bryan, some fifteen or twenty miles from Washington. His first visit to the capital had been in 1854, but now they became frequent. In 1856, in the Smithsonian Library he first saw Laplace's "*Mécanique Céleste*." "About December, 1856, I received a note from [Mr. J. E. Hilgard, assistant in charge of the Coast Survey Office], stating that he had been talking about me to Prof. Winlock, Superintendent of the '*Nautical Almanac*,' and that I might possibly get employment on that work. When I saw him again I told him that I had not yet acquired such a knowledge of physical astronomy as would be necessary for the calculations in question; but he assured me that this was no drawback, as formulæ for all the computations would be supplied me. I was far from satisfied at the prospect of doing nothing more than making routine calculations with formulæ prepared by others; indeed, it was almost a disappointment to find that I was considered qualified for such a place. I could only console myself by the reflection that the ease of the work would not hinder me from working my way up." The result was that one frosty morning in January, 1857, he took his seat in the office of the "*Nautical*

Almanac," at Cambridge, Mass. He was then in his twenty-second year. From this time onwards his career was one of unchequered brilliancy. In 1860, he went on an eclipse expedition up the Saskatchewan River. The weather was cloudy and nothing was seen of the eclipse.

In 1861, he was appointed Professor of Mathematics in the United States Navy, and as such he commenced transit instrument work at Washington Observatory on October 7.

Although he had been on an eclipse expedition in the previous year, he had never been inside an observatory, except on two or three occasions at Cambridge as a visitor. In September, 1863, he took charge of the mural circle. At this time it was usual at Washington for each observer to reduce his own observations. Newcomb contrived to introduce a uniform system of reduction in imitation of the system already introduced by Airy at Greenwich.

In October, 1865, the new transit circle arrived from Berlin. In the following years Newcomb succeeded in eradicating a vicious practice that obtained not only at his own observatory, but all over the world. He pointed out that clock stars ought only to be kept for place when at least a twelve-hour group has been obtained. For if an error depending on the sine or cosine of the right ascension exists in the clock star list, and observations only extend over six hours, the same error will be reproduced with only an infinitesimal degree of damping; whereas with twelve-hour groups the error is quickly damped out. In 1869, he observed an eclipse in Iowa, and in that year he began to turn his earnest attention to the problems presented by the moon's motion.

In 1870 he visited Europe for the first time, partly for an eclipse at Gibraltar that was obscured by cloud, and partly to search through the records of various observatories for seventeenth century observations of the moon.

In 1875 Newcomb was offered and declined the directorship of Harvard Observatory. On September 15, 1877, he took charge of the Nautical Almanac Office, a post which he held until his retirement in 1897.

The beginning of Newcomb's astronomical career coincided with the publication of Hansen's tables of the moon. These tables were an enormous advance on those previously in existence. Hitherto errors in computed coefficients had in many instances exceeded two or even three seconds of arc. Hansen's tables contain two or three errors in computed coefficients exceeding half a second of arc, but as a rule he attains a far greater accuracy.

The chief defect of the tables lies in the determination of the arbitrary constants, and in the omission of a whole group of planetary terms, the existence of which was not then suspected. A passage in Newcomb's autobiography throws much light on the cause of the former defect.

Hansen worked with the assistance of one computer only; this was no hardship while he was engaged on his theory. It would, in fact, require some management to assign work to a much larger staff simultaneously.

But when he came to compare his theory with observation and to determine his arbitrary constants, he was exceedingly short-handed. Instead, therefore, of making a detailed comparison with all existing observations, he based his comparison on a few years only. The result was utterly unworthy of his great theory. His parallax coefficient is two seconds in error, his principal elliptic term half a second in error, and so on. He also postulated a mechanical ellipticity in the moon's figure at least four times too large. With all these defects his tables mark an enormous advance, and his contemporaries believed that "our troublesome satellite has been at length reduced to order."

At the end of Newcomb's career the theory of E. W. Brown, which is to replace Hansen's, is complete, and tables based upon it are in the course of preparation. The advance upon Hansen will be greater than Hansen's advance upon his predecessors, and yet no one believes that the problem of the moon is solved.

Newcomb was in touch with all the work done in this period of fifty years, and great portions of this work were done by himself. His first investigation connected with the moon was a redetermination of the elliptic elements of the moon's orbit.

In this paper he brought to light an empirical term that is now known as the Jupiter evection term. It manifested itself as a fluctuation in the moon's eccentricity and perigee with a period of seventeen years. Some years earlier Airy had analysed eighty years of observations, and had been almost within touch of this term, but had wrongly identified the period as that of the moon's node, nineteen years.

Newcomb at this time did the bulk of his own computing, and to this fact his superior success is plainly due.

The explanation of the term was quickly assigned by Nevill to the action of Jupiter. At a time when most astronomers hardly realised that Hansen's tables needed correction, Nevill was being the pioneer in a new branch of the lunar theory.

The question of planetary inequalities was subsequently taken up by G. W. Hill, by Radau, by Newcomb himself and by E. W. Brown. It may now be considered as worked out. At this point we may notice one other contribution of Newcomb's to the gravitational theory of the moon, viz.: a beautiful theorem for obtaining the secular accelerations resulting from the secular diminution of the eccentricity of the earth's orbit round the sun.

Hansen, like Laplace, had assigned 12 seconds as the secular acceleration of the moon's mean motion; Adams had shown that this quantity was twice too large; but Adams' accuracy was not immediately admitted.

Some years later Newcomb produced his theorem, and again quite recently E. W. Brown, with the help of Newcomb's theorem, has practically reproduced Adams' value, which by that time was generally accepted, in a paper so short and simple that one wonders how there could ever have been any controversy on the subject.

We turn now to Newcomb's work of comparison of observations with theory.

His great work entitled "Researches on the Motion of the Moon" secured for its author the Copley Medal of the Royal Society.

In the first section he considers the ancient and mediæval eclipses. He rejects the solar eclipses, he ignores the magnitudes of lunar eclipses; and he shows the times of the lunar eclipses to be fairly consistent among themselves and with a secular acceleration slightly greater than the theoretical.

He assigns the excess to tidal friction. This no doubt is a *vera causa*, but there is at present no independent measure of its magnitude. In the concluding part of the "Researches" he gives the results of occultations observed in the century preceding 1750. These occultations were not only worked up by Newcomb, but actually extracted by him from the archives of European observatories. He has since extended his series of occultations down to 1898 and the results were published early this year. The older occultations required immense diligence. The observers' hieroglyphics had to be collected in many cases, in order to decipher their meaning. Clock errors had to be obtained in any way that was possible. Finally taking all the other quantities as known, a somewhat rough determination of the moon's mean error of longitude is obtained. From that it appears that in the moon's observed motion there exists a term unknown to theory with a period of about three hundred years.

To Newcomb, and to him alone, we owe such knowledge as we have of the moon's motion in the century preceding 1750. In his autobiography, Newcomb says: "One curious result of this work is that the longitude of the moon may now be said to be known with greater accuracy through the last quarter of the seventeenth century than during the ninety years from 1750 to 1840." The reductions for the latter period leave very much to be desired, but Newcomb's remark is too drastic. For instance, Newcomb has with his occultations traced an empirical term of sixty years' period back to 1820; before that date it is lost in the accidental error of his material. That term can be traced in the meridian observations back to 1750.

Newcomb's 'Researches' also contain the first recognition of the error of Hansen's mean motion of the moon's node. He deduces his correction by a comparison of an eclipse of 1715 with transit observations in or about 1868. Although the time interval is large, the position of the node on the first occasion is subject to much uncertainty.

The exact measurement of this motion is of great interest in view of the discrepancy from theory exhibited by the perihelion of Mercury.

Turning now to planetary theory, Newcomb's first paper was an investigation on the orbits of minor planets, with the object of ascertaining whether an explosion of a single planet could be assigned as their origin.

If such an explosion really took place, and if all secular changes affecting asteroids were already recognised, it would be possible to assign the place and time of the catastrophe; and the date, if obtained at all, would be obtained with an exactness unparalleled in other speculations as to the past

history of the universe. Unfortunately, Newcomb's conclusions were negative.

At this time Leverrier was still working out his theory of the larger planets, going outwards from the sun. He had not yet reached Uranus and Neptune, so Newcomb took up the orbits of these two planets, and also of their satellites, in order to determine their masses.

He also made a series of observations for this special purpose, and his work was rewarded with the Gold Medal of the Royal Astronomical Society.

Before the close of his life Newcomb had constructed tables for all the larger planets, and in addition for the minor planet Polyhymnia, in order to determine the mass of Jupiter. G. W. Hill relieved him of "about the most difficult [part] in the whole work—the theory of Jupiter and Saturn. Owing to the great mass of these 'giant planets,' the inequalities of their motion, especially in the case of Saturn, affected by the attraction of Jupiter, are greater than in the case of the other planets.

"Leverrier failed to attain the necessary exactness in his investigation of their motion. . . . [G. W. Hill] laboured almost incessantly for about ten years when he handed in his manuscript of what now forms Volume IV of the 'Astronomical Papers.'"

Newcomb followed Leverrier's methods in essentials. "Two systems of computing planetary perturbations had been used, one by Leverrier, while the other was invented by Hansen. The former method was, in principle, of great simplicity, while the latter seemed to be very complex and even clumsy. I naturally supposed that the man who computed the direction of the planet Neptune before its existence was known must be a master of the whole subject, and followed the lines he indicated.

"I gradually discovered the contrary, and introduced modified methods, but did not entirely break away from the old trammels.

"Hill had never been bound by them, and used Hansen's method from the beginning. Had he given me a few demonstrations of its advantages I should have been saved a great deal of time and labour."

Possibly in order that his own work, regarded as a verification of Leverrier's, might be quite independent, Newcomb introduced some changes into the calculations.

Leverrier, for instance, used the mean longitudes of the planets. Newcomb used the mean anomalies. Leverrier develops algebraically, according to the mean angles, and then reduces to arithmetical values. Newcomb develops algebraically in eccentric anomalies, reduces to number, and then transforms to mean anomalies arithmetically in each separate case. In a later volume he gives algebraic formulæ for the mean anomalies. He has enormously improved Leverrier's notation by introducing an operator that he terms "D."

When the final perturbations are compared, we are struck by how little Leverrier left for his successors. When allowance is made for the difference in the assumed masses of the planets, the difference in the perturbations calculated by Leverrier and Newcomb respectively are not such as could be

detected by observation. Newcomb has, however, improved the arbitrary constants, he has used the same planetary masses throughout all the tables, and finally he has enormously reduced the labour required for an ephemeris by, following the methods used by Hansen for the moon.

Like the lunar theory, the planetary theory is not yet perfect. The principal outstanding problems are :—

- (i) A centennial motion of forty seconds in the perihelion of Mercury, and
- (ii) the orbit of Mars.

Since Leverrier's time, the adopted solar parallax has increased by nearly three per cent. and consequently the mass of the earth by eight per cent.

Mars is the planet whose tabular orbit is most affected by an erroneous mass of the earth ; but although Newcomb was able to avail himself of the more accurate value of the mass of the earth, his tables of Mars are far less satisfactory than any other of his tables, and the problem has not yet been solved.

The discordance from theory in the motion of the perihelion of Mercury had been discovered by Leverrier from a discussion of the transits of Mercury.

Newcomb went over the ground again, with a little added material, and asking an additional question, "Are the errors of Mercury so related to those of the moon as to suggest that the earth is not a perfect timekeeper?" he found that he was not able to assert that such a relation existed.

Newcomb's Fundamental Catalogue and his "Astronomical Constants" must be mentioned, as well as his determination of Precession. These are great works in themselves, but to Newcomb mainly incidents in the thorough discussion of the motion of the moon and of the planets.

It was Newcomb also who assigned the lengthened period of latitude-variation to want of rigidity in the earth.

Newcomb visited Europe for the last time in 1908. Soon after his return his friends heard that he was hopelessly ill. He still continued his interest in his work, and passed through the press his last paper on the Moon.

He died on July 16, 1909, at the age of seventy-four. Twenty-two years had he spent in darkness before he became an astronomer, and subsequently the congenial nature of his work made the world for him one of "sweetness and light."

P. H. C.

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